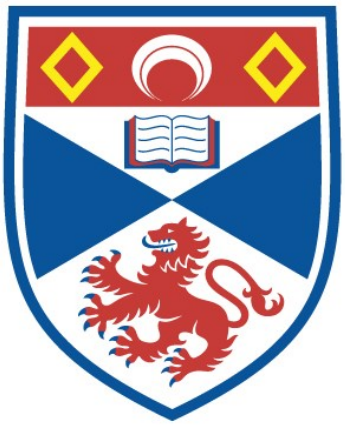
STUDIES OF 6A-THIATHIOPHTHENES 1,6,6A-TRISELENAPENTALENES AND RELATED SYSTEMS

Michael George Jackson

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



1973

STUDIES OF 6a-THIATHIOPHTHENES,

1,6,6a-TRISELENAPENTALENES,

AND RELATED SYSTEMS

being a Thesis

presented by

MICHAEL GEORGE JACKSON, B.Sc.,

to the

University of St. Andrews

in application for

THE DEGREE OF DOCTOR OF PHILOSOPHY.

3rd copy

To my dear wife, Eileen

and our daughter, Stephanie.

IN MEMORY OF MY FATHER

DECLARATION

I declare that this thesis is based on the results of experiments carried out by me, that it is of my own composition, and has not been submitted previously in application for a higher degree.

26th February 1973

CERTIFICATE

I hereby certify that Michael George Jackson, B.Sc. has spent eleven terms at research work under my supervision, has fulfilled the conditions of General Ordinance No. 12 (St. Andrews), and is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

Director of Research

UNIVERSITY CAREER

I entered the University of St. Andrews in October, 1964 and subsequently graduated B.Sc. with Upper Second Class Honours in Chemistry in June, 1968.

From October, 1968 until July, 1971 I carried out the work which is embodied in this thesis in the Department of Chemistry, St. Salvator's College, University of St. Andrews under the supervision of Dr. D.H. Reid.

ACKNOWLEDGEMENTS

It is with pleasure that I thank Dr. D.H. Reid for his advice and guidance, and for continued interest in this work.

I should like to express my gratitude to Professor Lord Tedder for making available laboratory facilities.

Thanks are also due to the technical staff of the Department of Chemistry for valuable assistance, to Mrs. P. Cooper, who prepared the typescript, and to Mrs. L. Hardwick of Allen and Hanbury's Ltd. for assistance with the diagrams.

Finally, I should like to thank the Awards Committee of the Senate of the University of St. Andrews for the award of a Research Studentship which enabled me to carry out this research.

CONTENTS

PART ONE: INTRODUCTION

SUMMARY

Reaction of hydrogen selenide with 1-methyl(ene)-1,3-diones in ethanolic hydrogen chloride containing iron(III) chloride affords either bis(3-methyl(ene)-1,2-diselenolium)tetrachloroferrates (II) or tris(1-methyl(ene)-1,3-diselenato)iron(III) complexes, and 2,4,6,8-tetraselenaadamantanes. Bis(3-methyl(ene)-1,2-diselenolium) tetrachloroferrates (II) are readily converted into the corresponding perchlorates. Dimethylthioformamide condenses with both 3-methyl(ene)-1,2-diselenolium perchlorates and tris(1-methyl(ene)-1,3-diselenato) iron (III) complexes to give 3-(2-dimethylaminovinyl)-1,2-diselenolium (Vilsmeier) salts. These salts react with sodium hydroxide to form 3-acylmethylene-3H-1,2-diselenoles, with sodium hydrogen sulphide to give 1-thia-6,6a-diselenapentalenes, and with sodium hydrogen selenide to form 1,6,6a-triselenapentalenes. In addition, treatment of 3-(2-dimethylamino-1-methylvinyl)-4-methyl-1,2-diselenolium perchlorate with sodium hydroxide, sodium hydrogen sulphide, and sodium hydrogen selenide affords 3,5-dimethyl-4H-pyran-4-selenoketone, 3,5-dimethyl-4H-thiopyran-4-selenoketone, and 3,5-dimethyl-4H-selenopyran-4-selenoketone respectively. 3,5-Dimethyl-4H-selenopyran-4-selenoketone is hydrolysed to 3,5-dimethyl-4H-selenopyran-4-one in wet chloroform solution. As a dry crystalline solid, 3,5-dimethyl-4H-selenopyran-4-selenoketone is atmospherically oxidised to 3,5-dimethyl-4H-selenopyran-4-one, 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole, and 3,4-dimethyl-1,6-dioxa-6a-selenapentalene. 3,4-Dimethyl-1,6,6a-triselenapentalene and 4,5-dihydro-3H-benzo[cd]1,6,6a-triselenapentalene are formed by treatment of 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole and 3-formyl-5,6-dihydro-4H-benzo[c]1,2-diselenole respectively with phosphoryl chloride

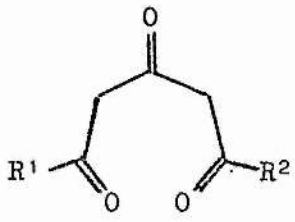
in dimethylformamide and subsequent addition of aqueous potassium selenosulphate or potassium selenotrithionate. Compounds containing oxygen and selenium atoms in the 1- and 6-positions of the 6a-selenapentalene ring, when treated with phosphorus pentasulphide, form 1,6-dithia-6a-selenapentalenes provided the 2- and 5-positions are unsubstituted.

The structures of 3-acylmethylene-3H-1,2-diselenoles and 1-thia-6,6a-diselenapentalenes are discussed in relation to spectroscopic data and compared with those of 3-acylmethylene-3H-1,2-dithioles and 6a-thiathiophthenes respectively. The crystal structures of 6a-thiathiophthene, 1,6-dithia-6a-selenapentalene, and 1,6,6a-triselenapentalene are compared and the structures of 1,6-dithia-6a-selenapentalenes and 1,6,6a-triselenapentalenes are discussed in relation to spectroscopic data. A bicyclic structure containing an oxygen-selenium-oxygen bonding sequence is proposed for 3,4-dimethyl-1,6-dioxa-6a-selenapentalene on the basis of its N.M.R and I.R. spectra.

The mechanism of the rearrangement of 6a-thiathiophthenes by aqueous sodium sulphide to 4H-thiopyran-4-thiones has been studied with sodium sulphide-S-35. The initial step in the rearrangement is a reductive cleavage of a sulphur-sulphur bond forming an anion which is then susceptible to nucleophilic attack by sulphide ion at the 2- (and/or 5-) position(s).

PART ONE

INTRODUCTION



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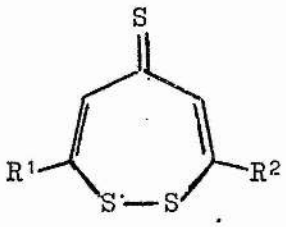

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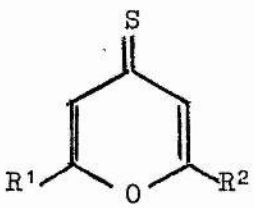

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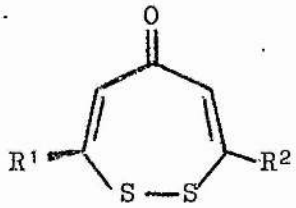

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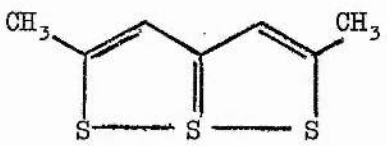

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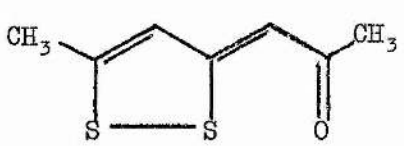

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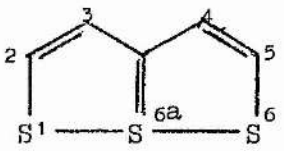

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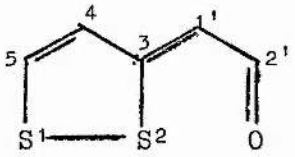

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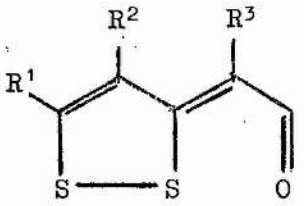

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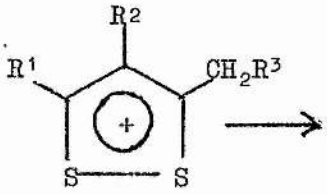

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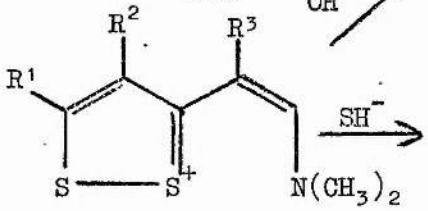

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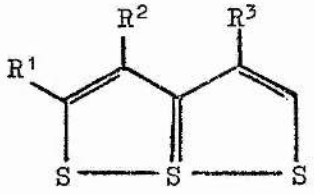

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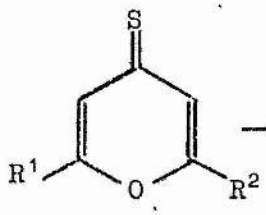

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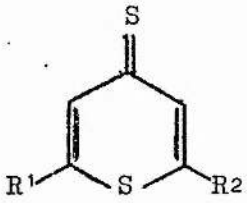

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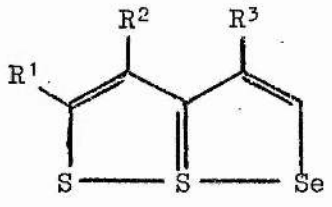

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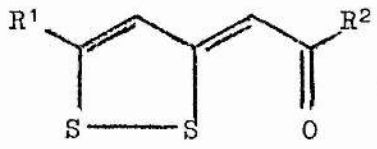

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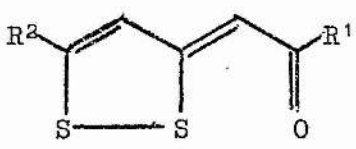

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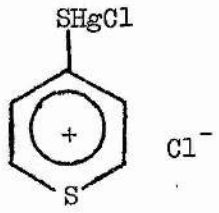


XVII

CHAPTER I

6a-Thiathiophthenes and Related Compounds

Arndt,[1] and later Traverso,[4,5] isolated orange to red crystalline compounds from the reaction between 1,3,5-triketones (I) and phosphorus pentasulphide to which the 1,2-dithiepin-5-thione structure (II) was assigned by Arndt. Yellow compounds were also obtained, either by the action of concentrated acid on the thione (II)[2] or by treating 4H-pyran-4-thiones (III) with alkali metal sulphide or hydrosulphide,[3-6] to which the analogous keto structure (IV) was assigned. The N.M.R. spectrum[7] of compound (IIa) appeared to confirm Arndt's structure. This showed two singlets in the ratio 3:1 demonstrating the C_{2v} symmetry of the molecule in solution. It was not until 1958 however that the correct geometry (V) and (VI) for these compounds was established from X-ray measurements by Bezzi and co-workers[8,9] and independantly from an I.R. study of the ketone (IVa) by Guillouzo[10] which showed a highly polarised carbonyl stretching frequency inconsistent with a structure such as (IV). Since that time, much interest has been centred on the 6a-thiathiophthene system, mainly concerned with the unique structural and bonding features of the molecule. The synthesis and structural studies in recent years of analogues of this system containing nitrogen, oxygen, and selenium atoms has contributed much to the understanding of the basic structure.

(1) Reviews.

Reviews on 6a-thiathiophthenes have been written by the following authors: Breslow and Skolnik,[11] Lozac'h and Vialle,[12] Lozac'h,[13]

Beer,[14] Klingsberg[17] and Reid.[19]

(2) Nomenclature.

Formula (VII) and the corresponding nomenclature for the system, 6a-thiathiophthene, suggested by Behringer,[20] will be used throughout this work. The nomenclature 1,6,6a-S^{IV}-trithiapentalene, suggested by Lozac'h,[13,21] is also in current use. Chemical abstracts indexes the system as [1,2]-dithiolo-[1,5-b][1,2]-dithiole-7-$S.^{IV}$ The oxygen analogues (VIII) will be called 3-acylmethylene-3H-1,2-dithioles.

CHAPTER II

Syntheses of 6a-Thiathiophthenes

Selected syntheses of 6a-thiathiophthenes are given in this section. These syntheses are preparatively useful, being extremely general, and lead to simply substituted 6a-thiathiophthenes. A natural extension of these syntheses is the incorporation of selenium into the 6a-thiathiophthene system. A route to selenium analogues making use of the Vilsmeier reaction has been developed and will be discussed in Part Two of this thesis.

(1) From 1,3,5-Triketones.

The first synthesis of a 6a-thiathiophthene involved the reaction between diacetylacetone and phosphorus pentasulphide.[1,2] This reaction has been applied to three other triketones by Traverso.[4,5] Stavaux and Lozac'h,[22] using a large number of triketones, report yields ranging between 5 and 55%.

(2) From 3-Methylene-1,2-Dithiolium Salts.

The methyl(ene) group in the 3-position of the 1,2-dithiolium ring (IX) is acidic[23] and has been condensed with N,N-dimethylthioformamide assisted by acetic anhydride or phosphoryl chloride to give the Vilsmeier salt (X).[15,18,24,25] Solvolysis of the Vilsmeier salt with aqueous hydroxide[15,18,24] yields the 3-acylmethylene-3H-1,2-dithiole (XI), with aqueous hydrosulphide[15,18,24] gives the 6a-thiathiophthene (XII) and in one case with aqueous sodium hydrogen selenide,[24] a selenium analogue (XIII) was obtained. A number of new 6a-thiathiophthenes having alkyl groups in the 2- or 3,4-positions have thus been synthesised in

excellent yield.

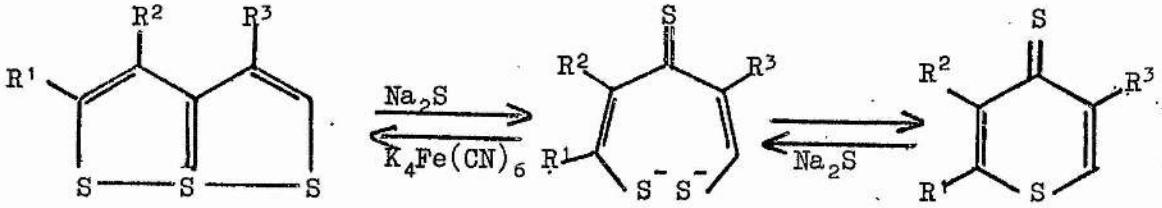
(3) From 4H-Pyran-4-Thiones.

Traverso[3-6] found that treatment of 4H-pyran-4-thiones (XIV) with alkali metal sulphide or hydrosulphide afforded the 3-acylmethylene-3H-1,2-dithiole (XVI) in addition to the expected product, 4H-thiopyran-4-thione (XV). The 3-acylmethylene-3H-1,2-dithiole formed (XVI a or b) depended on the nature of the substituents R^1 and R^2. Reaction of the 3-acylmethylene-3H-1,2-dithiole (XVI) with phosphorus pentasulphide then gave the 6a-thia-thiophthene. Alkaline hydrolysis of the mercuric chloride complex of 4H-thiopyran-4-thione (XVII) converted it into the parent 3-acylmethylene-3H-1,2-dithiole (VIII) from which the unsubstituted 6a-thiathiophthene (VII) was obtained by reaction with phosphorus pentasulphide.[26]

(4) From 4H-Thiopyran-4-Thiones.

The conversion of 6a-thiathiophthenes (XVIII) into 4H-thiopyran-4-thiones (XX) by treatment with sodium sulphide in aqueous dimethylformamide has been described.[29] Anions of type (XIX) were postulated as intermediates. The reverse sequence, involving ring opening of 4H-thiopyran-4-thione (XXa) by sulphide anion in dimethyl sulphoxide gave the dianion (XIXa). Intramolecular oxidative coupling of this dianion in situ, by potassium ferricyanide afforded the parent heterocycle in 49% yield.[27,28] The symmetrically substituted 2,6-diphenyl- and 3,5-dimethyl-4H-thiopyran-4-thiones were also converted into the corresponding 6a-thiathiophthenes in yields of 25% and 22% respectively.[28] Other unsymmetrically substituted 4H-thiopyran-

4-thiones gave only negligible yields of the corresponding 6a-thiathiophthene.



XVIII

XIX
a) $R^1=R^2=R^3=H$

XX
a) $R^1=R^2=R^3=H$

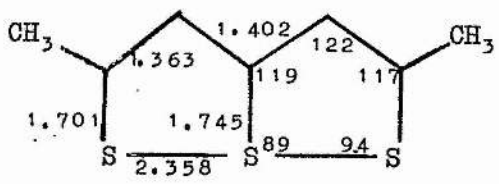


Fig. 1

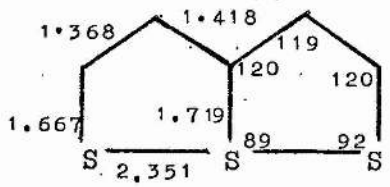


Fig. 2

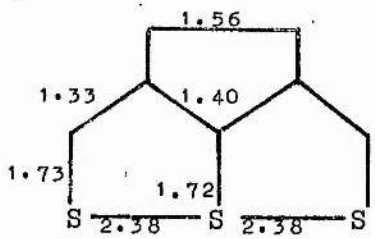


Fig. 3

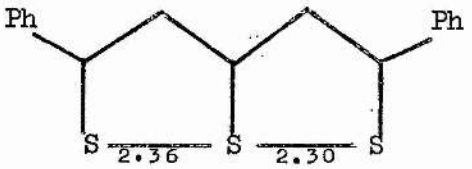


Fig. 4

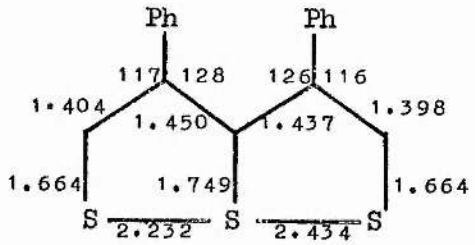


Fig. 5

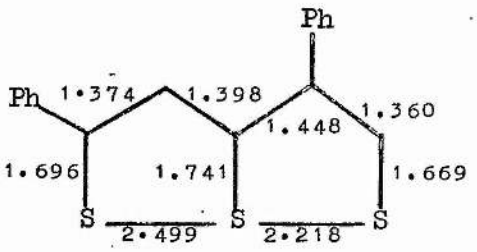


Fig. 6

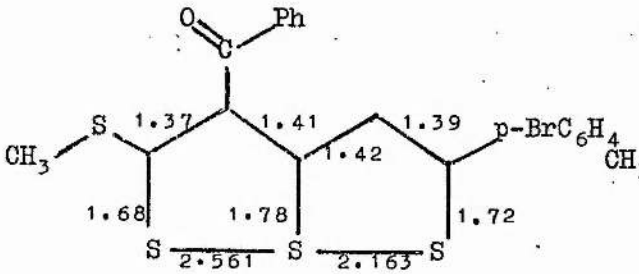


Fig. 7a

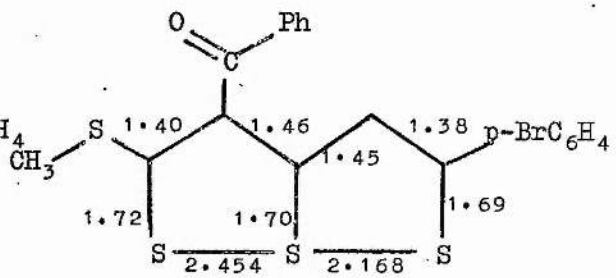


Fig. 7b

CHAPTER III

Structural Studies of 6a-Thiathiophthenes

The tools used in organic structure determinations, particularly X-ray crystallography and spectroscopic techniques, have been applied in the study of 6a-thiathiophthenes. These techniques have shown the positions of the individual atoms in the molecule, values have been obtained for bond distances and bond angles, and information on the magnetic equivalency of ring protons and substituents has been obtained. However, questions have arisen concerning the interpretation of these structural studies which have not yet been fully resolved.

(1) X-Ray Crystallography.

The crystal structure data for 2,5-dimethyl-6a-thiathiophthene (fig. 1) shows[8,9,30] that the molecule is planar and symmetrical about the central carbon-sulphur bond. The three sulphur atoms are collinear and equally spaced at a distance of 2.358Å; longer than the value (2.10Å) found for a cis-planar disulphide group[31] but significantly shorter than the sum of the van der Waals radii of two sulphur atoms (ca. 3.7Å, table 1). The ring carbon-carbon bonds (1.363 and 1.402Å) are almost equivalent and similar to the value (1.397Å) found in benzene. The lateral carbon-sulphur bonds (1.701Å) lie between that of a carbon-sulphur single bond (1.81Å) and a carbon-sulphur double bond (1.61Å) (table 1). The central carbon-sulphur bond (1.745Å) is somewhat shorter than a carbon-sulphur single bond (1.81Å). There is clearly a high degree of interaction in the system. The molecular structure of the parent heterocycle (fig. 2) has recently been determined by Hordvik.[42] The molecular dimensions are very similar to those of

2,5-dimethyl-6a-thiathiophthene and in fact it appears that crystals of 6a-thiathiophthene are isomorphus with those of 2,5-dimethyl-6a-thiathiophthene and the thiathiophthene systems are isostructural. X-ray crystallographic data[43] for 5,6-dihydrocyclopenta[cd]6a-thiathiophthene (fig. 3) also shows a symmetrical structure with equal sulphur-sulphur distances.

An investigation of the structure of the symmetrically substituted 2,5-diphenyl-6a-thiathiophthene by Hordvik[36] shows slightly unequal sulphur-sulphur distances (fig. 4). The 3,4-diphenyl isomer (fig. 5) has very unequal sulphur-sulphur distances[37] although the molecule is symmetrically substituted. This result can probably be attributed to the steric clashing of the phenyl substituents in the 3,4-positions. The thiathiophthene ring is effectively planar, but the bond angles external to the ring at carbons-3 and-4 deviate appreciably from 120°. The two phenyl rings also make angles of 70° and 74° with the best plane through the thiathiophthene ring.

The crystal structures of several unsymmetrically substituted 6a-thiathiophthenes have been determined[32-35,38,39] (figs. 6-9). The sulphur-sulphur bonds in these molecules are not equivalent but still longer than twice the covalent radius of a sulphur atom and much shorter than twice the van der Waals radius of sulphur (table 1). The molecular structure of 3-benzoyl-5-p-bromophenyl-2-methylthio-6a-thiathiophthene (fig. 7), reported by Paul,[34,35] shows that there are two crystallographically independant molecules in the crystal unit. Several bond lengths in one molecule differ markedly from the corresponding bond lengths in the other molecule, particularly in the disubstituted ring (figs. 7a and 7b). The sulphur-sulphur distances in

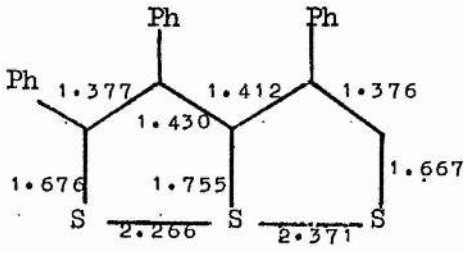


Fig. 8

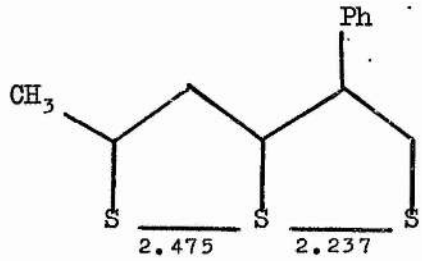


Fig. 9

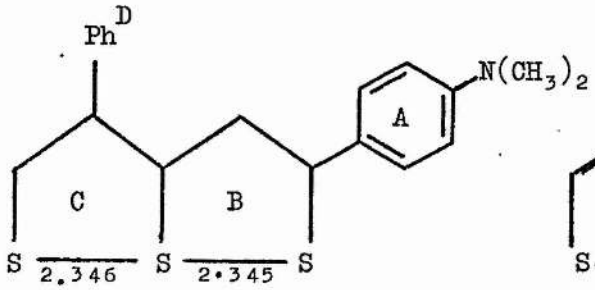


Fig. 10a

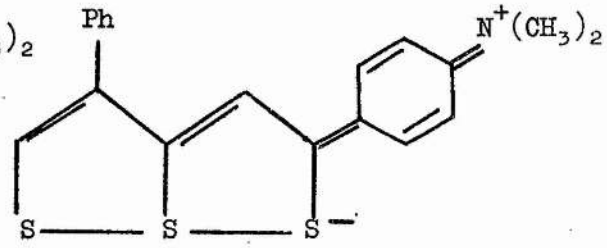


Fig. 10b

Covalent Bond	Sum of Covalent Bond Radii, A°	Sum of van der Waals radii, A°
C-C	1.54	3.06
C=C	1.33	
C"C (benzene)	1.397	
S-S	2.08	3.70
C-S	1.81	3.38
C=S	1.61	
S-O	1.70	3.25
C-O	1.43	2.95
C=O	1.29	
C-N	1.47	3.03
S-N	1.74	3.35
N-O	1.36	2.90
C-Se	1.94	3.53
C=Se	1.73	
Se-O	1.83	3.40
Se-S	2.21	3.85
Se-Se	2.34	4.00

Table 1. Ref. 71

2,3,4-triphenyl-6a-thiathiophthene (fig. 8) have been found[38] to be very similar to those of 3,4-diphenyl-6a-thiathiophthene (fig. 5). Also, the exchange of the 2-phenyl group for a methyl group[39] in 2,4-diphenyl-6a-thiathiophthene[32,33] leaves the bonding in the sulphur sequence almost unchanged (figs. 6 and 9).

Hordvik[41] has examined the structure of 2-p-dimethylaminophenyl-4-phenyl-6a-thiathiophthene and finds equal sulphur-sulphur distances although the molecule is unsymmetrical (fig. 10a). There is an angle of 5° between the plane of ring B and the plane of ring C. The phenyl groups A and D are 14° and 81° respectively out of the plane of the thiathiophthene nucleus. It is apparent from the bond lengths that electron donation from the dimethylamino group leads to contributions from structures such as that shown (fig. 10b).

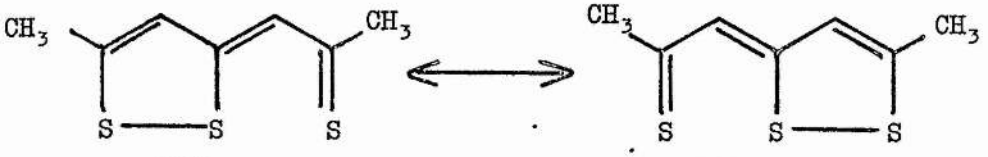
In view of the ambiguity of the results of 2,5-dimethyl-6a-thiathiophthene, which could represent the average of two-fold disorder of molecules with a 'short' and a 'long' sulphur-sulphur bond (XXI a and b), it has been suggested[34,35] that there is a short sulphur-sulphur distance of 2.12-2.22 Å and a long sulphur-sulphur distance of 2.47-2.57 Å irrespective of the substituents. Hordvik's[36] investigation of the structure of 2,5-diphenyl-6a-thiathiophthene, which has sulphur-sulphur distances of 2.36 and 2.30 Å (fig. 4), suggests that the two sulphur-sulphur distances in a symmetrical 6a-thiathiophthene are exactly equal in an isolated molecule. It is apparent, however, that the sulphur-sulphur bonds in the 6a-thiathiophthene system, due to the diminished bond order from unity, are particularly sensitive to both the intermolecular and intramolecular environment. Nyburg[40] has re-examined

the structure of 2,5-dimethyl-6a-thiathiophthene with a full three-dimensional refinement of the P_{nma} structure. No doubling of peaks was found on the electron density distribution and the anisotropic thermal parameters of all atoms had normal magnitudes. He thus finds no prima facie evidence for statistical disordering in the structure, suggested by several authors,[34,35,67] and concludes that if there is disordering, the difference in the two molecular geometries (XXI a) and (XXI b) is too small to be detected by X-ray structure analysis. Refining the data for the alternative P_{n2a} space group resulted in excessive asymmetry and unacceptable bond lengths.

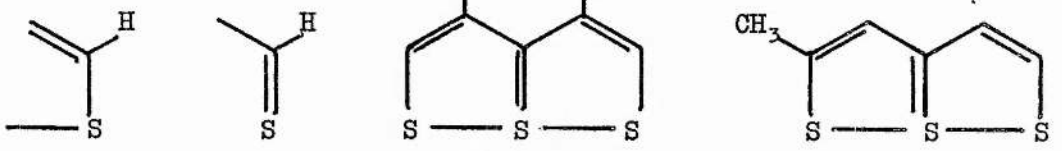
It should be noted that, whereas the difference of the sulphur-sulphur bond lengths in a 6a-thiathiophthene may be as large as 0.4 Å (fig. 7a), the sum of the sulphur-sulphur distances in all the 6a-thiathiophthenes studied is almost constant, from a minimum of 4.622Å (fig. 7b) to a maximum of 4.724Å for the same compound (fig. 7a). This excludes the value of 4.76Å for 5,6-dihydrocyclopenta[cd]6a-thiathiophthene (fig. 3) as the ethano bridge is likely to pull carbons -3 and-4 closer together thus increasing the length of the three-sulphur distance.

(2) Nuclear Magnetic Resonance Spectroscopy.

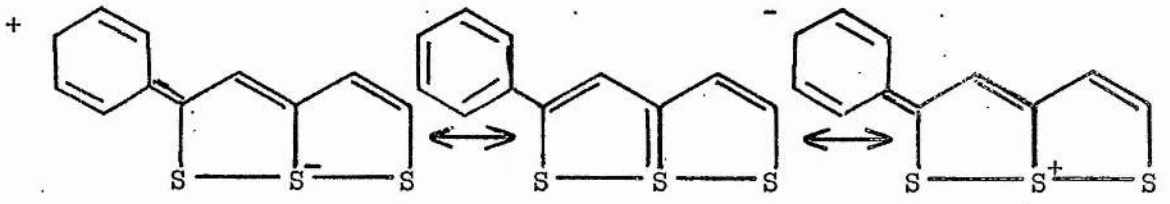
The early N.M.R. study of 2,5-dimethyl-6a-thiathiophthene[7] showed the symmetry of the system and further papers confirm this symmetry and give more information.[24,25,44-48] Pinel, Mollier and Lozac'h[46] have estimated that the ring current in 2,5-dimethyl-6a-thiathiophthene is 65% of that in naphthalene. Dingwall, McKenzie and Reid have compared



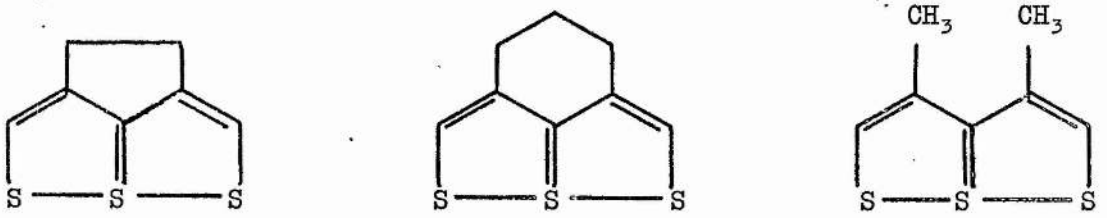
XXI a XXI b



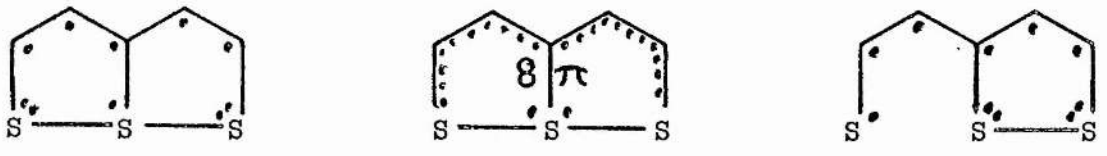
XXIIa XXIIb XXIII XXIV



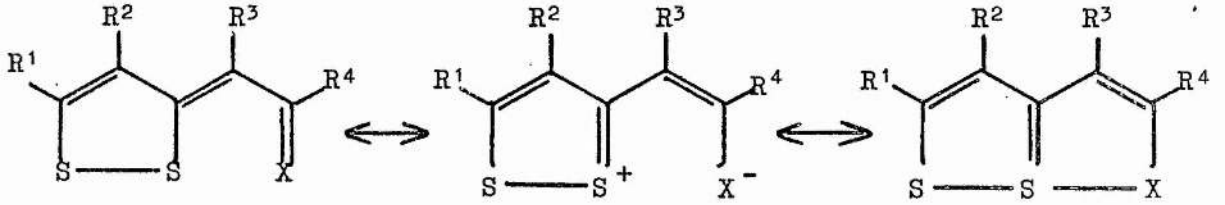
XXV



XXVI XXVII XXVIII



XXIX XXX XXXI



XXXII XXXIII XXXIV

the chemical shift of the thioformyl proton in heterocyclic thioaldehydes with that of a proton in the 2- or 5-position of the 6a-thiathiophthene nucleus.[24] The chemical shift of the thioformyl proton in heterocyclic thioaldehydes[49,155] is normally in the region δ 10.4-11.2, and that even when the thioformyl group is highly polarised in the sense =CH-$S^{\ominus}$ it does not fall below δ 10.2. The chemical shift of H-2 (or H-5) in 6a-thiathiophthenes[24] is normally in the region δ 8.6-9.3 and is, therefore, consistent with being in the environment (XXII a) rather than (XXII b). It has also been shown[24] that the ring protons H-2, H-3 and H-4 of the 6a-thiathiophthenes are much more deshielded than the corresponding protons in the oxygen counterparts. For the series of compounds studied, $\Delta\delta$ for H-2 lies in the range 0.71-1.07; for H-3, 0.48-0.77; and for H-4, 0.96-1.07. This is evidence of a greater ring current and aromaticity in the 6a-thiathiophthenes. Symmetrical 6a-thiathiophthenes show magnetic equivalence of ring protons or identical substituents at the pairs of sites C-2, C-5 and C-3, C-4 demonstrating that in solution, in which intermolecular effects are averaged, the sulphur-sulphur bonds are of equal length. Thus, the N.M.R. spectrum of 3,4-diphenyl-6a-thiathiophthene (XXIII) shows[15] a symmetrical structure although in the crystalline state the sulphur-sulphur bonds are of unequal length[37] (fig. 5).

(3) X-Ray Photoelectron Spectroscopy.

Clark has recently reported[50] the application of X-ray photoelectron spectroscopy in a study of the structure of 6a-thiathiophthenes. The sulphur core binding energies (2s and 2p) for 2,5-dimethyl-6a-thiathioph-

thene (V) and the parent heterocycle (VII) are split into a 2:1 doublet in accord with the X-ray crystallographic data,[40,42] and the values indicate that the central sulphur core electrons are considerably more tightly bound than those for the equivalent terminal sulphur atoms. By contrast, the sulphur molecular core binding energies for the 3,4-diphenyl derivative (XXIII) indicate three types of sulphur, consistent with an unsymmetrical structure in agreement with the X-ray crystallographic study.[37] The measured core binding energies for 2-methyl-6a-thiathiophthene (XXIV), for which no X-ray data is available, also indicate three types of sulphur atom. This could be interpreted as being due to a structure with unequal sulphur-sulphur bonds, or to electronic pertubation of a symmetrical structure by the methyl substituent. Calculations on 2-methyl-6a-thiathiophthene, using a similar ring geometry to that of 2,5-dimethyl-6a-thiathiophthene, show that the effect of replacing hydrogen by methyl in a symmetrical thiathiophthene structure is quite small. This result is not compatible with the experimental results and he concludes that 2-methyl-6a-thiathiophthene has a structure with unequal sulphur-sulphur bonds.

(4) Electron Spin Resonance Spectroscopy.

The E.S.R. spectra of radical anions of three symmetrical 6a-thiathiophthenes and one nitrogen isostere have been obtained.[51] These results are consistent with a plane of symmetry passing through the central carbon-sulphur bond and vertical to the plane of the molecule. The π-spin population distribution found is in accord with that to be expected using as a model the electron-rich three-centre bond,[52] which is discussed

in Chapter IV.

(5) Electronic Spectroscopy.

The ultraviolet and visible spectra of 6a-thiathiophthenes[15,20,22] show strong absorption bands near 260 nm. and 500 nm., the latter being responsible for the orange to deep red colours of these compounds. The presence of a phenyl group in the 2-position introduces a further band at about 320 nm. whereas a phenyl group in the 3-position causes little change in the spectrum. In 2,4-diphenyl-6a-thiathiophthene, the X-ray structural analysis[32,33] shows the 2-phenyl group to be twisted 25^{o}, and the 4-phenyl group 52^{o} out of the plane of the thiathiophthene nucleus. Thus, conjugation of type (XXV) is likely for the 2-phenyl substituent but impossible for the 4-phenyl substituent. An anomalously large red shift (ca. 30 nm.) observed for the ethano bridged thiathiophthene (XXVI),[15] when compared with the corresponding propano thiathiothphene[15] (XXVII) and 3,4-dimethyl-6a-thiathiophthene[18] (XXVIII), can be explained by postulating a strain effect causing a distortion of the π-electronic system. This has been confirmed by X-ray crystallography data[43] (fig. 3) where the sum of the sulphur-sulphur distances (4.76 Å) is the largest recorded for a 6a-thiathiophthene.

(6) Infra-Red Spectroscopy.

Studies by Pietra, Garbuglio and Mammi[55] of several 6a-thiathiophthenes and some oxygen and selenium containing analogues, point out the aromatic character of the unoxygenated compounds by the presence of bands at 1465, 850 and 700 cm^{-1}. The electronic configuration of

6a-thiathiophthenes shifts towards a highly conjugated carbonylic system when one sulphur atom is replaced by oxygen. Replacement of sulphur in the 6a-thiathiophthene system by selenium causes little change in the spectra. A further I.R. study[56] of 6a-thiathiophthenes in different solvents shows the absence of a vibration due to a thiocarbonyl group. The authors conclude that the spectra are in accord with a delocalised 10 π electron aromatic system.

(7) Electron Polarisation Spectroscopy.

The electronic polarisation spectrum of 2,5-dimethyl-6a-thiathiophthene[54] has recently been determined. To interpret the experimental results, SCF-CI calculations of the PPP type have been carried out for the models (XXIX), (XXX) and (XXXI) using only p-orbitals. The experimental results are only explained if the equilibrium structure corresponds to the unsymmetrical model (XXXI). However, since approximations have been used in some of the parameters in the theoretical calculations, the suggestion is that not too much emphasis should be placed on these results.

(8) Dipole Moments.

The dipole moments of a number of 6a-thiathiophthenes and their oxygen and selenium analogues have been reported.[46,57,58,139] Lozac'h[46] has stated that the contribution of the more important limiting forms (XXXII), (XXXIII) and (XXXIV) for a given compound depends very largely on the nature of X and the substituents. The dipole moments of the 6a-thiathiophthenes (X=S) have been found to be smaller than the corresponding

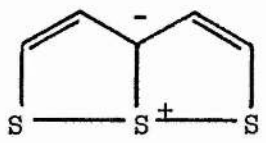
3-acylmethylene-3H-1,2-dithioles (X=O) indicating that structures such as (XXXIV) are more important for the 6a-thiathiophthenes and structures such as (XXXIII) are more important for the 3-acylmethylene-3H-1,2-dithioles.

CHAPTER IV

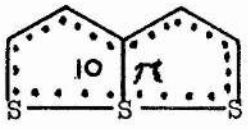
Theories of Bonding in 6a-Thiathiophthenes

Various models and theories have been proposed to describe the electronic distribution in the unique 6a-thiathiophthene structure. Early descriptions by Giacometti and Rigatti[59] and Shustorovich[60] based on the "one-bond, no-bond" resonance concept (XXI) have been studied by the molecular orbital method and assume that the d-orbitals of the central sulphur atom take no part in bonding.

Lozac'h[21] proposed a model (XXXV) in which the central sulphur atom utilises two sp_x-hybrid orbitals for bonding to the lateral sulphur atoms; the $3p_y$-orbital is used in bonding to the central carbon atom and the $3p_z$-orbital contains the unshared pair of electrons. The carbanionic atom has the usual sp^2-hybridisation, the lone pair occupying a p-orbital. By utilising a d-orbital of the central sulphur atom,[16] the covalent structure (XXXIV, X=S) could be achieved. A calculation[53] of the electronic structure of 2,5-dimethyl-6a-thiathiophthene using the semi-empirical ASMO SCF method, excluding the contribution of d-orbitals, has shown that for a quantitative discussion a consideration of d-orbitals is essential. Maeda[61] employed such a model in which one 3p-orbital and one 3d-orbital of the central sulphur atom are hybridised to give two pd-orbitals at 180° to each other. The hybrid orbitals form σ-bonds by overlap with 3p-orbitals of the lateral sulphur atoms. One of the remaining 3p-orbitals of the central sulphur atom is involved in σ-bonding with the central carbon atom. The remaining electron in a p-orbital, together with one p-electron from



XXXV



XXXVI

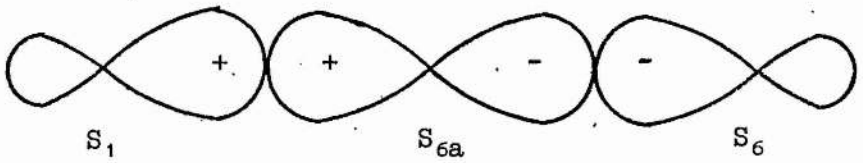


Fig. 11

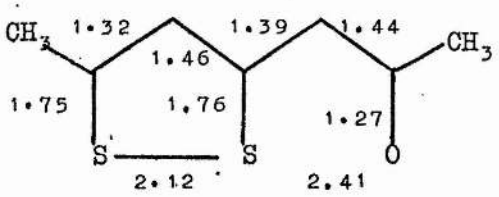


Fig. 12

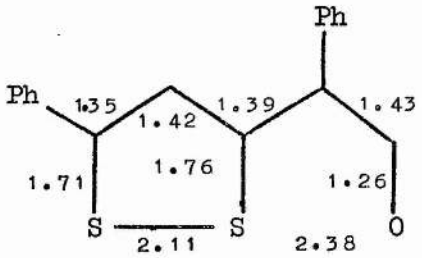
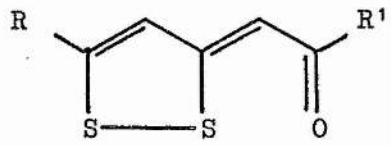
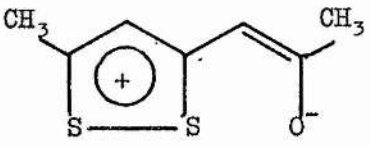


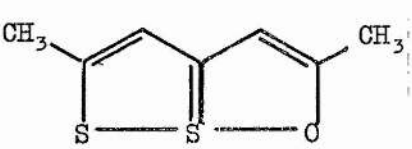
Fig. 13



XXXVII

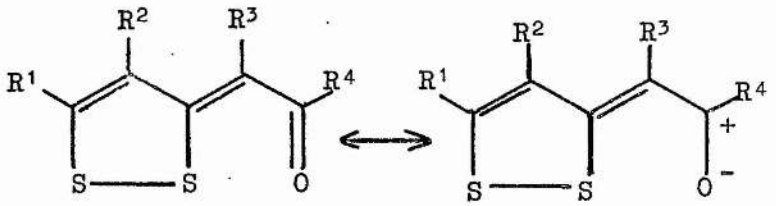


XXXVIII

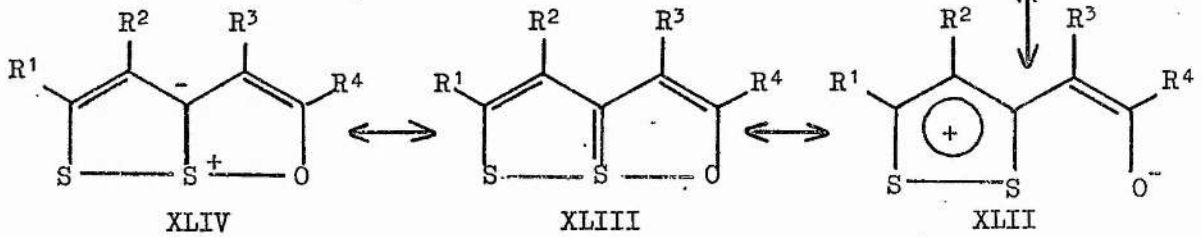


XXXIX

	R	R¹
a)	CH_3	CH_3
b)	Ph	Ph
c)	p-$CH_3OC_6H_4$	Ph
d)	Ph	p-ClC_6H_4
e)	Ph	p-$CH_3OC_6H_4$



XL XLI



XLIV XLIII XLII

each sp^2-hybridised carbon atom and two electrons from each lateral sulphur atom contribute a total of ten electrons forming a delocalised π-electron system which confers aromatic character upon the molecule (XXXVI). Calculations, however, of overlap integrals[62] gave only negative overlap of the pd-hybrid orbitals on the central sulphur atom with the adjacent sulphur 3p-orbitals. In a later paper[63] he was able to show that strong positive overlap could occur by postulating that 3d-orbital contraction on the central sulphur atom took place caused by the charge distribution around the molecule. SCF MO calculations using a ten π-electron model similar to that of Maeda[61,62,63] have been carried out[66] to predict the π-electron transitions and ionisation potentials expected from structure (XXXVI) for 6a-thiathiophthene, the 2,5-diphenyl- and the 2-methyl-5-phenyl- derivatives. There is satisfactory agreement between predicted and experimental transition energies and ionisation potentials, and it is concluded that π-bonding exists between the three sulphur atoms.

Gleiter and Hoffmann[52] have made a notable contribution to theories of bonding in 6a-thiathiophthenes. Their theory is to regard the three sulphur atoms as a linear system using three orbitals occupied by four electrons for σ-bonding (fig. 11) with π-bonding superimposed. This type of bonding has been proposed for the interhalogen compounds[64] and has also been studied in the transition state for an S_N2 displacement at a saturated carbon atom[65]. The further stabilisation conferred on the electron-rich 3-centre bond by the π-electron system is not expected to be great since the equilibrium distance for a 3-centre bond is reached at a stage where pπ-pπ overlap is still small. Calculations of the potential energy of the

three-sulphur sequence were carried out when the central sulphur atom is displaced towards the lateral sulphur atoms. These show a clear preference for an unsymmetrical structure when 3d-orbitals are not utilised and a nearly symmetrical and very flat minimum of ca. 0.3 Å when 3d-orbitals are included. Their result is in good agreement with crystallographic data for 6a-thiathiophthenes (figs. 1-10) which shows that the sum of the sulphur-sulphur distances in any 6a-thiathiophthene is almost constant (ca. 4.67 Å) but the difference of the sulphur-sulphur distances in a 6a-thiathiophthene may be as large as 0.4 Å.

Hordvik and his colleagues[32] have carried out theoretical calculations on 2,4-diphenyl-6a-thiathiophthene using as a model the three-centre, four-electron bond and find good qualitative agreement between the calculated bond orders and the experimental bond lengths. These authors have also suggested[32,41] a way of rationalising the different sulphur-sulphur bond lengths found in 6a-thiathiophthenes. From structural investigation and by theoretical calculations on the linear trihalide ions, it has been found[68] that the less electronegative of the terminal halogen atoms forms the strongest bond with the central halogen atom. Thus, the phenyl group in the 2-position of 2,4-diphenyl-6a-thiathiophthene (fig. 6) causes S_1 to be more electronegative than S_6 and hence S_1-S_{6a} is a longer bond than S_{6a}-S_6. Similarly, in the 3-acylmethylene-3H-1,2-dithioles, the less electronegative sulphur (compared with oxygen) forms the stronger, and hence shorter bond with the central sulphur atom. However, the structure of 2-methyl-4-phenyl-6a-thiathiophthene (fig. 9) shows that replacement of a phenyl group by a methyl group in the 2-position causes no appreciable

difference to the sulphur-sulphur distances. This is contrary to what would be expected on the basis of considerations of electronegativities.

The suggestion that 6a-thiathiophthenes exist as valence tautomers (XXI) on the basis of spectral evidence [69] does not appear to have been justified. The bonds in the linear three-sulphur sequence of 6a-thiathiophthenes are fractional in both σ- and π-character and so, being weaker than other bonds in the molecule, are more susceptible to changes in bond length if the σ-system, the π-system, or both are perturbed to some degree. This pertubation may be caused by the intermolecular, or intramolecular environment. It seems likely, on the above evidence, that the two sulphur-sulphur distances in any symmetrically substituted 6a-thiathiophthene are exactly equal in an isolated molecule, and the deviation from equality results from the bonds being unusually sensitive to intermolecular and intramolecular effects.

CHAPTER V

Analogues Based on the 6a-Thiathiophthene System

During the past few years, analogues of the 6a-thiathiophthene system have been synthesised in which the lateral sulphur atoms have been replaced by selenium, nitrogen or oxygen atoms and the central sulphur atom has been replaced by a selenium atom. X-ray crystallographic and spectroscopic techniques have shown that many of these analogues show interesting similarities to the 6a-thiathiophthene system and the question has arisen as to whether these analogues can be considered to be bicyclic systems similar to that of the 6a-thiathiophthenes.

(1) 3-Acylmethylene-3H-1,2-Dithioles.

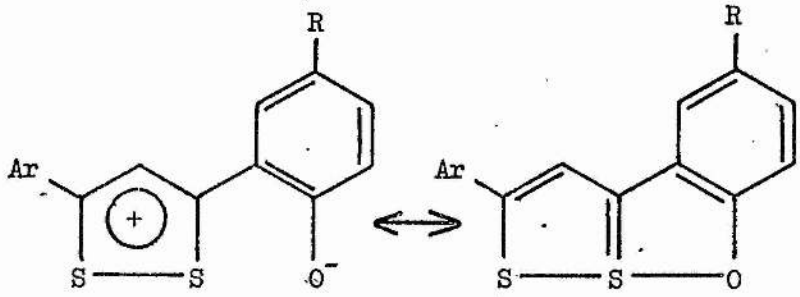
The structure of 3-(1-acetylmethylene)- 5 -methyl-3H-1,2-dithiole (VI) was first established from an infra-red study by Guillouzo[10] and the X-ray structure analysis (fig. 12) completed by Mammi[70] three years after the structure analysis of 2,5-dimethyl-6a-thiathiophthene. The crystal and molecular structure of 3-(1-formylbenzylidene)-5-phenyl-3H-1,2-dithiole (fig. 13) has also been determined[98] for a comparison with 2,4-diphenyl-6a-thiathiophthene. It can be seen from a comparison of the structures of the 3-acylmethylene-3H-1,2-dithioles (figs. 12 and 13) with the corresponding 6a-thiathiophthenes (figs. 1 and 6) that replacement of one sulphur atom by oxygen causes significant changes in the bond lengths. Also the bond lengths in the two oxygen compounds (figs. 12 and 13) are almost identical, whereas in the corresponding 6a-thiathiophthenes (figs. 1 and 6), changes

in the substitution pattern have considerably altered the bond lengths, especially in the three-sulphur sequence. The structures of both 3-acylmethylene-3H-1,2-dithioles are almost planar and the S-S...O sequence in both molecules is almost linear. The sulphur-sulphur distances, (2.12 Å and 2.11 Å), lie close to the value (2.10 Å) found for a cis-planar disulphide group.[31] The sulphur-oxygen distances are shorter than the corresponding van der Waals distance of 3.25 Å but longer than the sum of the covalent single bond radii for sulphur and oxygen[71] (1.70 Å). The carbon-carbon bonds in both molecules show definite alternation. The carbon-oxygen distances (1.27 and 1.26 Å) are comparable to the sum of the carbon and oxygen covalent double bond radii (1.29 Å, table 1).

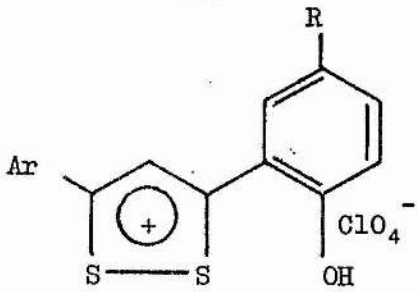
N.M.R. spectroscopy confirms the gross structure of the 3-acylmethylene-3H-1,2-dithioles;[24,44] thus the parent compound (VIII) and the ketone (VI) both show four signals. The 3-acylmethylene-3H-1,2-dithioles exhibit an aldehydic proton peak at δ 9.2 - 9.4 compared to the value (δ 9.5 - 10.0) normally found for aldehydic protons indicating that there is some sulphur-oxygen interaction.

Extended Hückel molecular orbital calculations have been carried out on the 3-acylmethylene-3H-1,2-dithiole (VI) and other structures having short sulphur-oxygen distances.[72] The results show that calculated sulphur-oxygen overlaps are close to zero, indicating that covalent bonding between sulphur and oxygen is negligibly weak. However, physical measurements by French workers, particularly of the infra-red spectra and dipole moments, of many 3-acylmethylene-3H-1,2-dithioles indicate that partial sulphur-oxygen bonding does exist and therefore these compounds can be

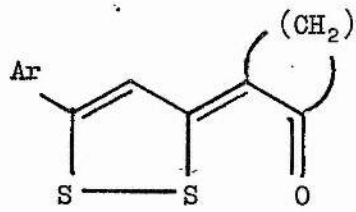
considered to be bicyclic systems. No absorption is observed in the usual carbonyl absorption region (1600-1750 $cm.^{-1}$) for these compounds. Lozac'h,[56,75] on the basis of solvent shift data, has assigned values in the region 1535-1562 $cm.^{-1}$ for the carbonyl absorption of the 3-acylmethylene-3H-1,2-dithioles (XXXVII b-e), whereas (XXXVII a) gives a carbonyl absorption at 1578 cm^{-1} (KBr) which corresponds to 76% C=O double bond character. This value suggests contributions from polarised forms such as (XXXVIII) and/or a structure having a sulphur-oxygen covalent bond such as (XXXIX). In later papers,[46,139] the electronic structure of the 3-acylmethylene-3H-1,2-dithioles is discussed in terms of contributions from the limiting forms (XL-XLIV), and the contribution of the more important limiting forms (XL), (XLII) and (XLIII) for a given compound has been found to depend very largely on the substituents. The position of the carbonyl absorption band in the infra-red spectrum can be taken as a measure of the contribution of the limiting form (XL) and hence as a measure of the sulphur-oxygen interaction. For certain compounds (XXXVII) this gives a value of ca. 70% C=O double bond character.[56] However, compounds such as (XLV) do not exhibit any band in the region 1500-1700 cm^{-1} which is displaced by solvent effects.[46] In fact the infra-red spectra of compounds (XLV) are analogous to the perchlorates (XLVII). In the region 1220-1290 cm^{-1} several absorption bands are found one of which (ca. 1250 cm^{-1}) is attributed to a C-O vibration coupled with the aromatic ring. This band is notably displaced by solvent effects. Such an absorption band at 1250 cm^{-1} attributed to a C-O vibration coupled with an aromatic ring, has also been observed[146] in the



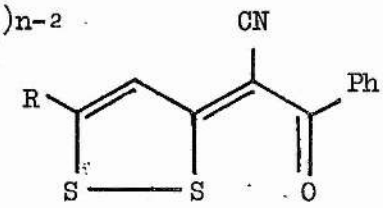
XLV XLVI



XLVII

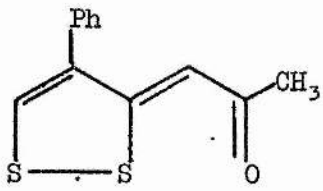


XLVIII

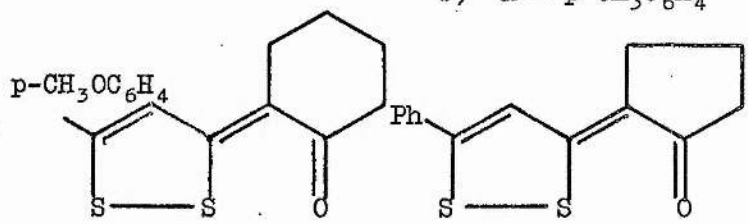


XLIX

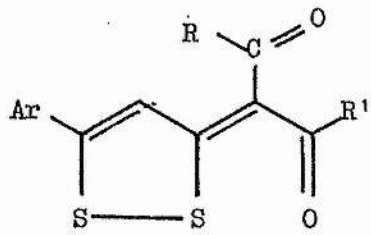
a) R = t-Bu
b) R = p-$CH_3C_6H_4$



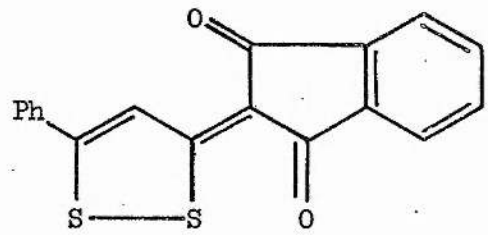
L



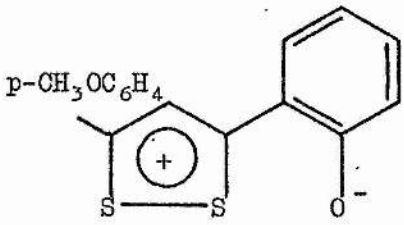
LI LII



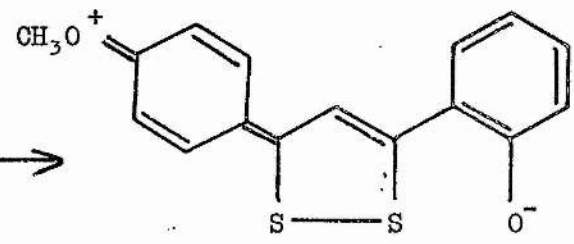
LIII



LIV

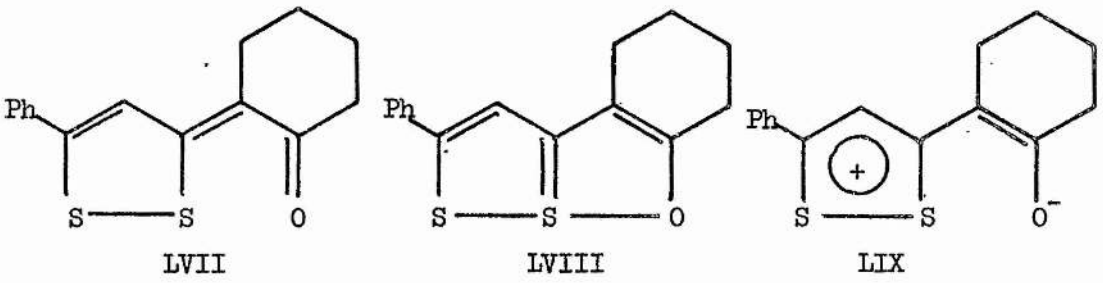


LV



LVI

case of benzofuran. These results are in accord with resonance between the limiting forms (XLV) and (XLVI), and hence a partial bond between the phenolic oxygen and the 2-sulphur of the 1,2-dithiole ring is indicated.[46] The structures of the cycloalkane compounds (XLVIII) have been studied[139] and also show sulphur-oxygen interaction. When n=5 the carbonyl absorption is situated at ca. 1620 cm^{-1}, but when n=6,7 or 8 the carbonyl absorption is lowered to between 1543-1567 cm^{-1}. The ketones (XLIX) and (L)[76], and (LI) and (LII)[139] containing oxygen enriched with ^{18}O have recently been synthesised. From a comparison of their infra-red spectra with those of the ^{16}O ketones, the authors assign to the carbonyl absorption ($\nu_{C=^{16}O}$) 1554 cm^{-1} for compound (XLIXa), 1549 cm^{-1} for compound (XLIXb), 1574 cm^{-1} for compound (L), 1558 cm^{-1} for compound (LI) and 1632 cm^{-1} for compound (LII). The observed isotopic displacement ($\nu_{C=^{16}O} - \nu_{C=^{18}O}$) for compound (LI) is 8.5 cm^{-1} whereas the calculated value for the isotopic displacement is 37.75 cm^{-1}, indicating that the carbonyl group here has only 22% double bond character.[139] Similarly, the observed isotopic shift of 16 cm^{-1} for (LII) indicates 40% double bond character of the carbonyl group. Thus these 3-acylmethylene-3H-1,2-dithioles are best represented by contributions from structures (XL), (XLII) and (XLIII). The dicarbonyl compounds (LIII) show absorption in the region 1600-1650 cm^{-1} assigned to the trans carbonyl group, as well as an absorption in the region 1535-1562 cm^{-1} attributed to the cis carbonyl group.[75] This latter absorption disappears when one oxygen is replaced by sulphur. In the indanedione derivative (LIV), interaction between sulphur and oxygen is reduced and more normal carbonyl absorptions (1640 cm^{-1}) are observed.


Ph
S
S
O
LVII
Ph
S
S
O
LVIII
Ph
+
S
S
O⁻
LIX

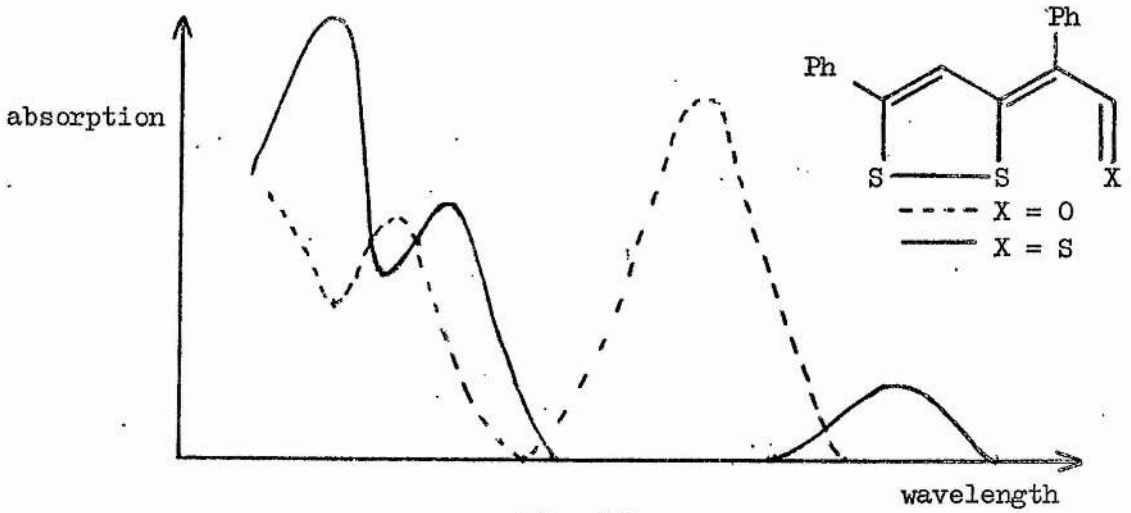
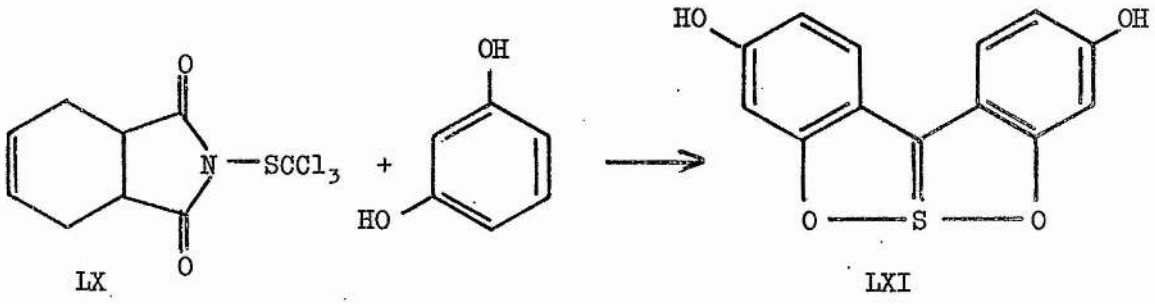
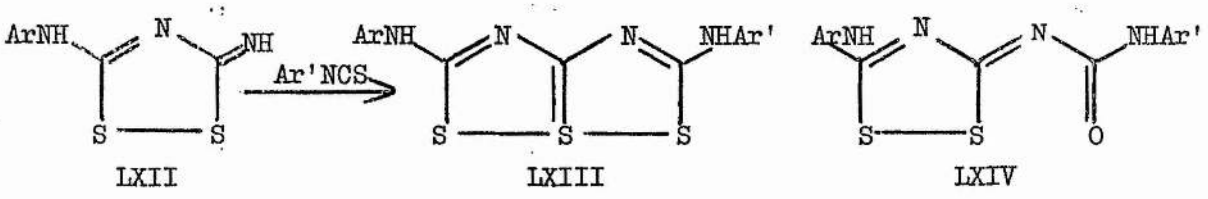
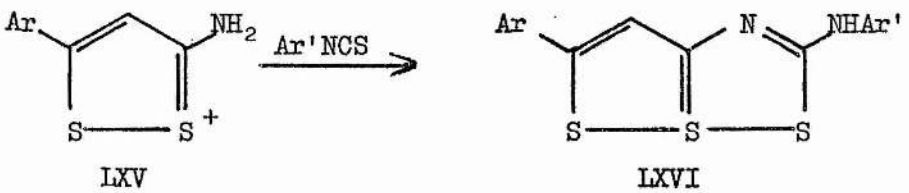

absorption
wavelength
Ph
Ph
S
S
X
X = O
X = S

Fig. 14


O
N
SCCl3
O
LX
+
OH
HO
HO
OH
O
S
O
LXI


ArNH
N
NH
S
S
LXII
Ar'NCS
ArNH
N
N
NHAr'
S
S
S
LXIII
ArNH
N
N
NHAr'
S
S
O
LXIV


Ar
NH2
S
S+
LXV
Ar'NCS
Ar
N
NHAr'
S
S
S
LXVI

The dipole moments of several 3-acylmethylene-3H-1,2-dithioles have been determined[46,57,58,139] and in general are higher than those of the corresponding 6a-thiathiophthenes. The determination of the dipole moment gives a measure of the contribution of forms such as (XLII). For compounds such as (XLV) the experimental value of the dipole moment is much less than that calculated for this structure,[46] and the authors conclude that forms such as (XLV) are not so important in describing the structure and forms with a covalent bond such as (XLVI) are more important. The higher dipole moment (4.96 D) found for compound (LV) compared with the value (4.40 D) found for compounds (XLVI, Ar=Ph, R=H,CH_3) can be explained by proposing polarised forms such as (LVI). Mollier has calculated[139] the dipole moments expected for structures (LVII), (LVIII) and (LIX) and obtains the values 5.1D, 3.65-3.74D, and 15.8D respectively. The experimental value of 4.18D. can only be explained if substantial contributions of the covalent bonded structure (LVIII) are involved in the electronic distribution.

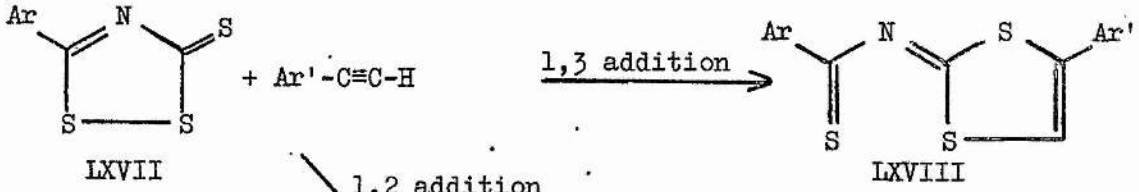
The ultra-violet and visible spectra of 6a-thiathiophthenes and their oxygen analogues bear a characteristic relationship to each other.[24,73,74] Thus, when the oxygen atom is replaced by sulphur (fig. 14), the visible absorption is shifted to longer wavelength and weakened and the ultra-violet absorption is shifted to shorter wavelength and greatly strengthened. The effect of replacing the oxygen atom of benzophenone by sulphur is to cause a bathochromic shift of all the bands, the short wavelength absorption being appreciably weakened. There is obviously more interaction in the three-sulphur 6a-thiathiophthene system than in the 3-acylmethylene-3H-1,2-dithiole system.

The evidence suggests that 3-acylmethylene-3H-1,2-dithioles cannot adequately be represented by formula (XL) and structures such as (XLII) and (XLIII) must be taken into account when describing their electronic structures.

Compound (LXI) has been identified as the product from fusion of resorcinol with the fungicide captan (LX).[77] No further details or spectral properties of this unusual compound have been reported as yet. The isolation of compound (LVII) and the strong evidence for its representation by structure (LVIII) suggests that a structure having a linear oxygen-sulphur-oxygen sequence should be stable.

(2) Aza-Analogues of 6a-Thiathiophthenes.

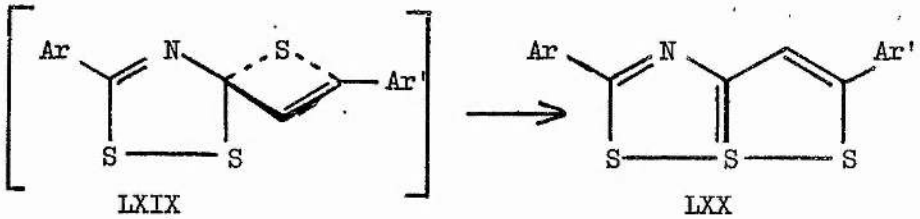
A number of compounds in which the CH group in the 3/4 position of the 6a-thiathiophthene ring has been replaced by nitrogen are known. The reaction of 5-imino-3-arylamino-1,2,4-dithiazoles (LXII) with aryl isothiocyanates gives products which are formulated as derivatives of 2,5-diamino-3,4-diaza-6a-thiathiophthene (LXIII).[74] Compounds (LXIII) and their oxygen analogues (LXIV) show a relationship in their ultraviolet spectra similar to that shown by 6a-thiathiophthenes and their oxygen analogues. Further resemblance to the 6a-thiathiophthene system is shown by the synthesis of a single 3,4-diaza-6a-thiathiophthene from isomeric starting materials (LXII , Ar=C_6H_5, Ar'=p-$CH_3O\cdot C_6H_4$ in Ar' NCS and vice-versa). Similarly, the reaction of 3-amino-5-aryl-1,2-dithiolium salts (LXV) with aryl isothiocyanates gives compounds which are formulated as derivatives of 3-aza-6a-thiathiophthene[78] (LXVI). Vialle has also obtained 3-aza-6a-thiathiophthenes (LXX) by the addition of aryl acetylenes



LXVII

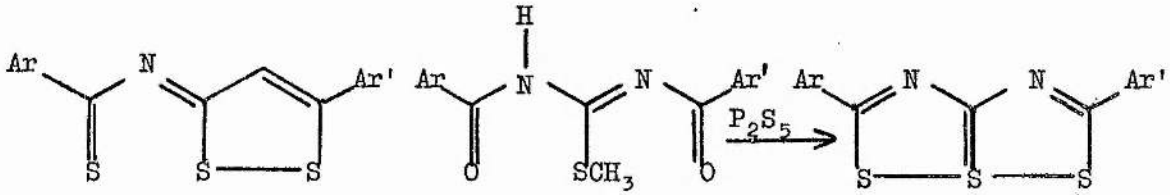
LXVIII

1,2 addition



LXIX

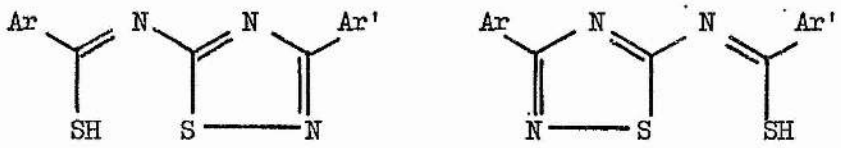
LXX



LXXI

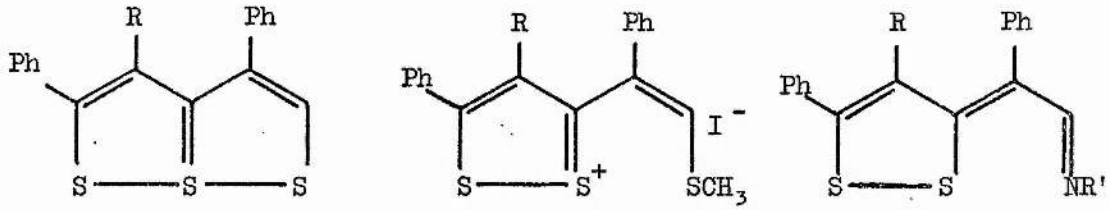
LXXII

LXXIII



LXXIV

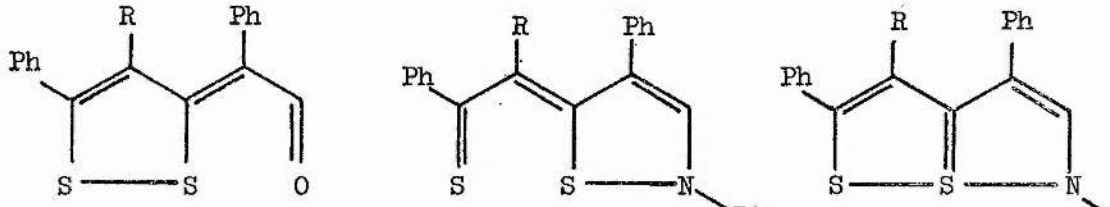
LXXV



LXXVI

LXXVII

LXXVIII



LXXIX

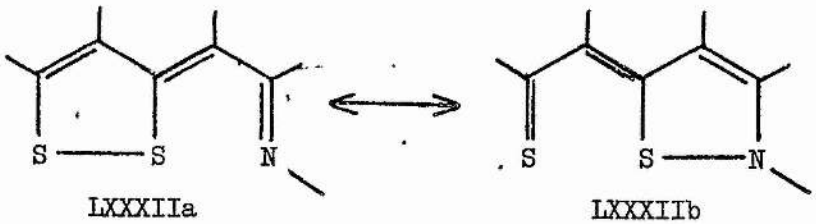
LXXX

LXXXI

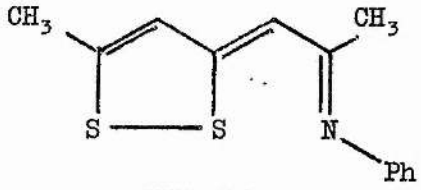
to 5-aryl-1,2,4-dithiazole-3-thiones[79] (LXVII). 1,3-Addition gives the 1,3-dithiole derivative (LXVIII), and 1,2-addition gives an intermediate (LXIX) which rearranges to the 3-aza-6a-thiathiophthene (LXX). The authors formulate these compounds as monocyclic systems (LXXI). The reaction of N,N-diaroyl-s-methyl-isothioureas (LXXII) with phosphorus pentasulphide gives 2,5-diaryl-3,4-diaza-6a-thiathiophthenes (LXXIII).[80,81] This system is formulated as bicyclic by the same authors since reaction of the diaza-6a-thiathiophthene with ammonia gives two isomers (LXXIV) and (LXXV) showing the equivalence of the lateral sulphur atoms.

(3) Nitrogen Analogues of 6a-Thiathiophthenes.

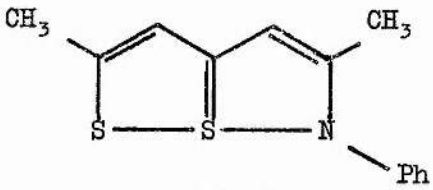
Methylation of the 6a-thiathiophthenes (LXXVI) gives the methiodides (LXXVII) which react readily with primary aromatic amines giving imines (LXXVIII).[82] The imines (LXXVIII) can also be obtained from the corresponding 3-acylmethylene-3H-1,2-dithioles (LXXIX) by reaction with primary amines. Behringer has also obtained similar compounds from the fluoroborates,[83] and Dingwall[15] from the Vilsmeier salts (X) by reaction with aqueous methylamine. Klingsberg does not discuss whether the imines (LXXVIII) exist as 1,2-dithioles (LXXVIII), isothiazoles (LXXX) or as bicyclic systems (LXXXI). Behringer has considered[83] possible structures for the imines and has ruled out the possibility of valence tautomerism (LXXXIIa $\longleftrightarrow$ LXXXII b) in view of the N.M.R. spectrum of compound (LXXXIII) which shows no change when the temperature is varied from -60° to $+120^{\circ}$. A monocyclic structure (LXXXIII) was thus preferred but the data does not exclude a bicyclic structure (LXXXIV). The crystal structure of a thiathiophthene nitrogen isomer (LXXXV) has recently been reported by Leung



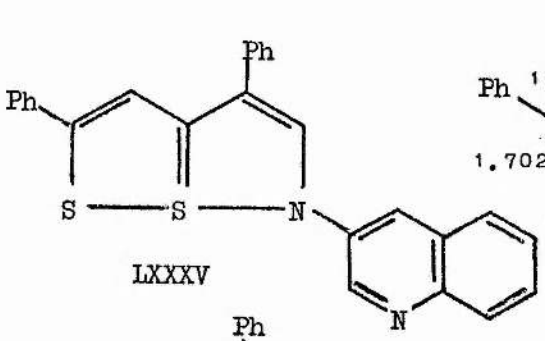
LXXXIIa LXXXIIb



LXXXIII



LXXXIV



LXXXV

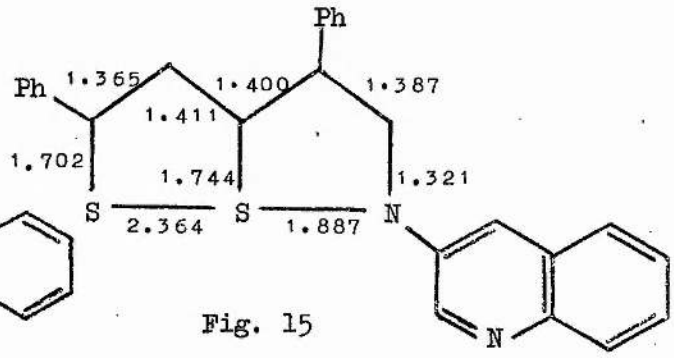
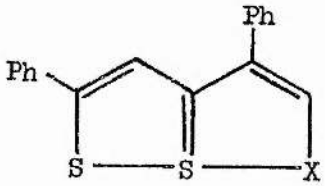
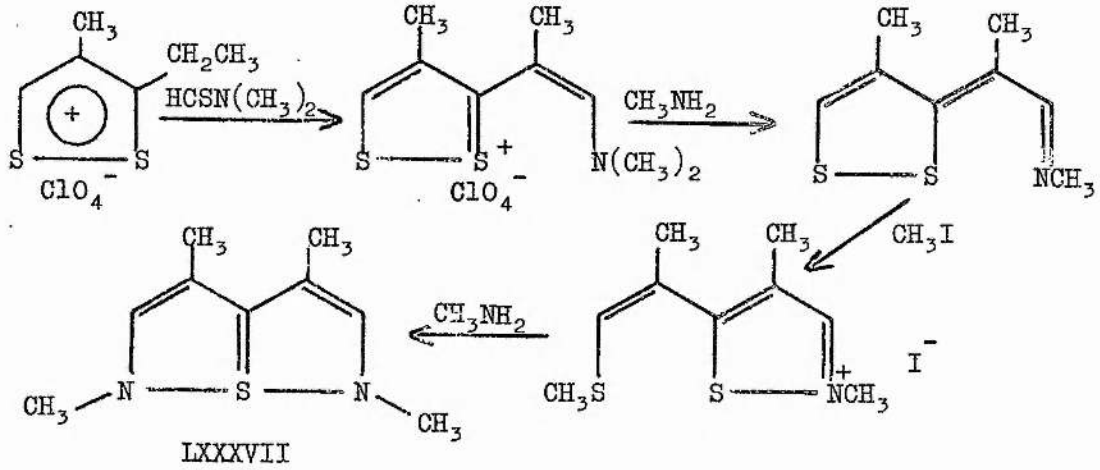


Fig. 15



LXXXVI

		Difference in Electronegativity	Sulphur-Sulphur Bond Length A°
a)	X = S	0.0	2.51
b)	X = Se	0.1	2.49
c)	X = NR	0.5	2.36
d)	X = O	1.0	2.09



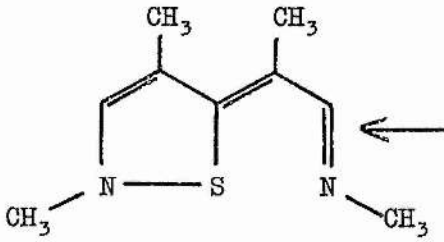
LXXXVII

Scheme 1.

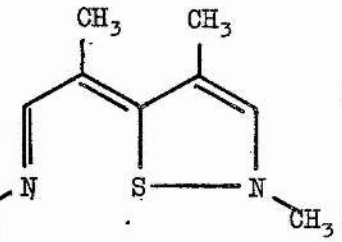
and Nyburg[84] after a preliminary communication[85]. It is found that the central nucleus of eight atoms (fig. 15) is almost planar, the maximum deviation being 0.03 Å from planarity. The sulphur-sulphur distance (2.364 Å) is similar to that found in several 6a-thiathiophthenes (figs. 1, 2, 4 and 8) and the sulphur-nitrogen distance (1.887 Å) is greater than the sum of the covalent radii (1.74 Å) but considerably less than the sum of the van der Waals radii (3.35 Å) of sulphur and nitrogen (table 1). The carbon-carbon bond distances are very similar to those of 2,4-diphenyl-6a-thiathiophthene (fig. 6). Structurally, this imine bears more resemblance to the corresponding 6a-thiathiophthene (fig. 6) than to the oxygen analogue (fig. 13) indicating that the bicyclic system (LXXXV) is significant. Leung and Nyburg have correlated[84] the difference in electronegativity between sulphur and X with the sulphur-sulphur bond distance for the four knownS-S-X systems (LXXXVI a-d). The sulphur-sulphur distance decreases as the difference in electronegativity[71] increases (cf. the linear trihalide ions[68]). On this basis however, since sulphur is slightly more electronegative than selenium, it would be expected that the sulphur-sulphur bond in the selenium analogue(LXXXVI b) would be longer than that found in the 6a-thiathiophthene (LXXXVI a).

(4) Isothiazolo [5,1-e] Isothiazoles.

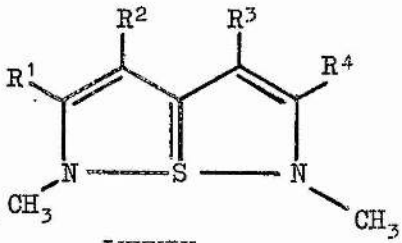
The symmetrically substituted isothiazolo [5,1-e] isothiazole (LXXXVII) has been synthesised by Reid and Symon[86] via the reaction sequence shown in scheme 1. The N.M.R. spectra of compound (LXXXVII) in deuteriochloroform, carbon disulphide and hexadeuteriodimethyl sulphoxide show only three sharp singlets, thus excluding a frozen monocyclic



LXXXVIIIa

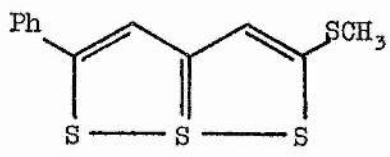


LXXXVIIIb

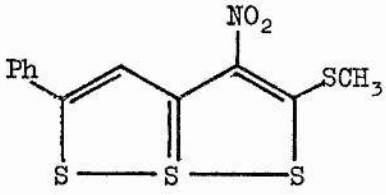


LXXXIX

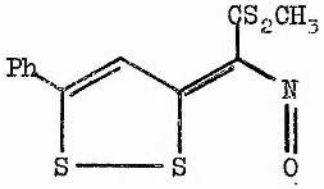
	R^1	R^2	R^3	R^4
a)	H	H	H	H
b)	CH_3	H	H	CH_3
c)	H	$-CH_2CH_2CH_2-$		H



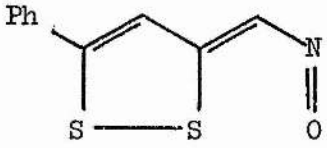
XC



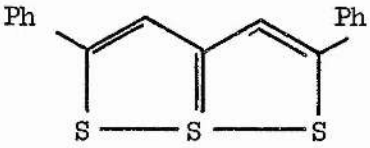
XCI



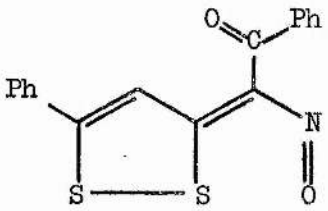
XCII



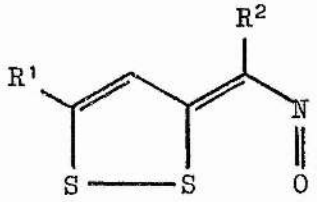
XCIII



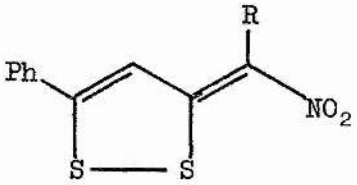
XCIV



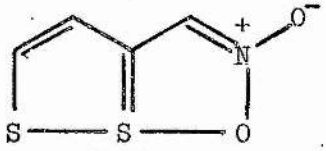
XCV



XCVI



XCVII



XCVIII

	R^1	R^2
a)	Ph	$CSN(CH_3)_2$
b)	CH_3S	CS_2CH_3
c)	Ph	NO_2

a) R = H
b) R = CH_3
c) R = Br

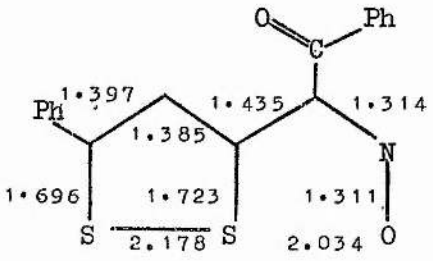


Fig. 16

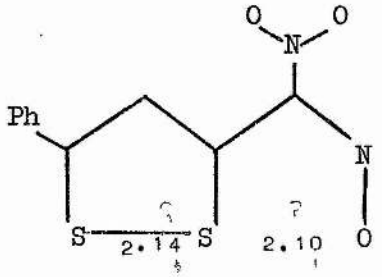


Fig. 17

structure (LXXXVIII a or b). No distinction between a bicyclic system (LXXXVII) and a system of rapidly interconverting valence isomers (LXXXVIII a ⟷ LXXXVIII b) can be made from the N.M.R. data. It is significant, however, that the N.M.R. spectrum of compound (LXXXVII) in carbon disulphide remained unchanged down to -70°. Three other symmetrically substituted isothiazolo [5,1-e] isothiazoles (LXXXIX a-c) have been synthesised[18] and a crystallographic study[87] of compound (LXXXIX c) shows the sulphur-nitrogen distances to be almost equivalent (1.90 and 1.94 Å). These bond lengths are very similar to the sulphur-nitrogen distance (1.887 Å) found in the imine (fig. 15). The near equivalency of the sulphur-nitrogen distances in (LXXXIX c), which are again longer than the sum of the covalent radii but considerably shorter than the sum of the van der Waals radii for sulphur and nitrogen (table 1), and the symmetry of the peri-dimethyl derivative (LXXXVII) at low temperature, supports the formulation of these compounds as bicyclic systems (LXXXIX) analogous to that now preferred for the 6a-thiathiophthenes.

(5) Nitro and Nitroso Thiathiophthenes.

In their studies of the reactivity of 6a-thiathiophthenes, Beer and co-workers[88,90] successfully nitrated 2-methylthio-5-phenyl-6a-thiathiophthene (XC) to give the nitro derivative (XCI). Nitrosation of compound (XC) however, and nitration or nitrosation of 2,5-diphenyl-6a-thiathiophthene (XCIV) gave compounds formulated as the nitroso compounds (XCII) and (XCV) on the basis of spectral evidence. Compound (XCII) was also converted into the simpler nitroso compound (XCIII). In later communications, three further nitroso compounds (XCVI a-c) are described[90] as well as the structurally related nitro compounds[89] (XCVII a-c).

The crystal and molecular structures of two nitroso thiathiophthenes[91] (XCV) and (XCVIc) and one nitro compound[92] (XCVIIc) have been completed after preliminary communications,[93,94] and structural data for these compounds are given (figs. 16, 17 and 18). Difficulty was encountered in the analysis of compound (XCVIc, fig. 17) as the crystals were invariably twinned. The nitroso compound (XCV, fig. 16) is significantly non-planar, the nitrogen atom being 0.054 Å from the best plane through the central nucleus of eight atoms. The very short sulphur-oxygen distance (2.034 Å) is 0.35 Å less than the shortest previously reported sulphur-oxygen distance (fig. 13). The sulphur-sulphur distance is larger than twice the covalent radius of a sulphur atom (table 1) and also longer than that found for the 3-acylmethylene-3H-1,2-dithioles (figs. 12 and 13). Substantial double bond character is indicated by the short carbon-nitrogen distance. On the basis of the molecular dimensions, the authors conclude that sulphur-oxygen bonding in the molecule is significant. The similar bond lengths found in compound (XCVIc, fig. 17) where the nitroso rather than the nitro group is adjacent to the dithiole ring, indicate that here, too, the presence of sulphur-oxygen bonding is significant. The bond lengths in the nitro compound (XCVII c, fig. 18) however, are more 'normal'. Thus the sulphur-sulphur distance is comparable to that of normal covalent sulphur-sulphur distances (table 1). The sulphur-oxygen distance is similar to that reported for the 3-acylmethylene-3H-1,2-dithioles (figs. 12 and 13), but considerably longer than that found in the nitroso derivatives (figs. 16 and 17). In a further parallel with the structure of the 3-acylmethylene-3H-1,2-dithioles, the nitro compound (fig. 18)

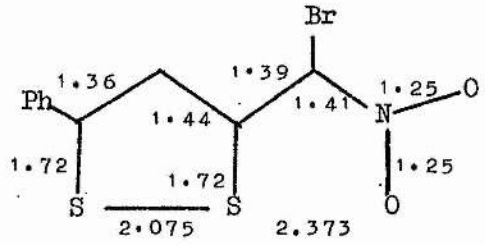
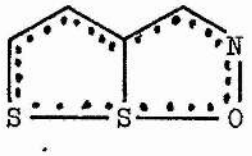
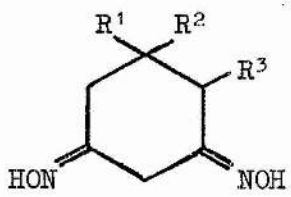


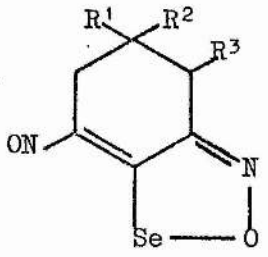
Fig. 18



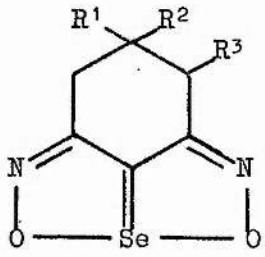
XCIX



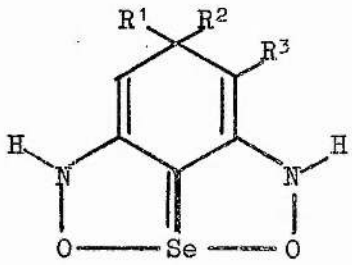
C



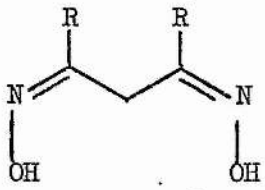
CI



CII

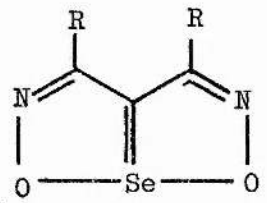


CIII



CIV

a) R = H
b) R = CH_3



CV

a) R = H
b) R = CH_3
c) R = $-CH_2CH_2CH_2-$
d) R = $-CH_2C(CH_3)_2CH_2-$

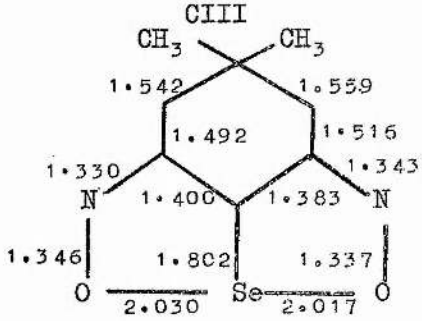
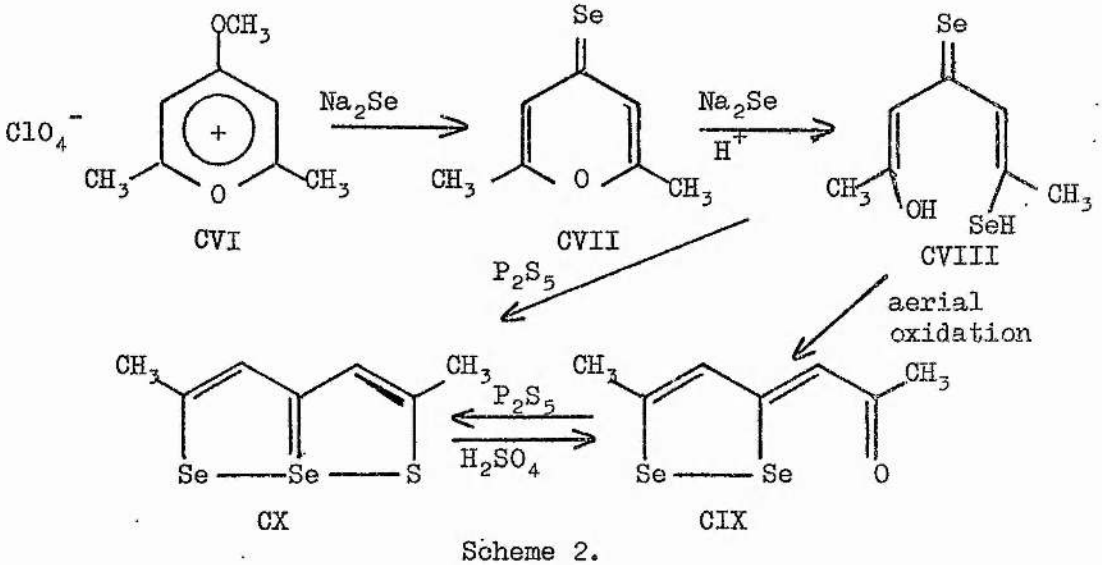


Fig. 19



CVI CVII CVIII CX CIX

Scheme 2.

exhibits alternate short and long carbon-carbon bonds, whereas the pattern of carbon-carbon bond lengths in the nitroso compound (fig. 16) is not so regular.

The authors conclude[91,92] that the nitroso group takes precedence over other groups (CO.Ph, $CS.SCH_3$, $CS.N(CH_3)_2$, NO_2) in competition for the apparently advantageous position adjacent to the dithiole sulphur-sulphur link. A resemblance to the 3-acylmethylene-3H-1,2-dithioles is shown by the nitro compounds (XCVII) and they are represented by a monocyclic structure (XCVII) with possible contributions from highly polarised structures. There is no evidence at present to suggest any sulphur-oxygen bonding (XCVIII) in these compounds. The nitroso compounds, however, appear to resemble 6a-thiathiophthenes more than 3-acylmethylene-3H-1,2-dithioles and bicyclic structures such as (XCIX) are probably significant.

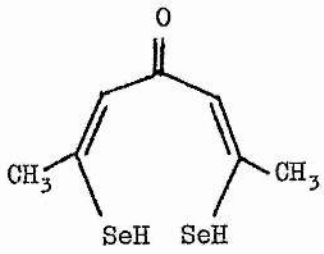
(6) [1,2,5] Oxaselenazolo[2,3-b][1,2,5]Oxaselenazoles-7-Se.[IV]

In 1949 King and Felton[95] obtained a series of stable red or orange organo-selenium compounds in the attempted oxidation of cyclohexane 1,3-dione dioximes (C) with selenium dioxide, to which they attributed the structure (CI). Structures (CII) and (CIII) were rejected on strain considerations. Vialle[96] has repeated this reaction on two symmetrical cyclohexane 1,3-dione dioximes and also on the dioximes of the β-diketo compounds (CIVa and b). The N.M.R. spectra of the four compounds (CV a-d) show the equivalency of the peri-positions in solution and moreover, the spectrum of the parent compound (CV a) shows only a singlet from $+40^{\circ}$ to -60°. The spectrum[97] of compound (CVd) at room temperature shows two sharp singlets, indicating rapid oscillation

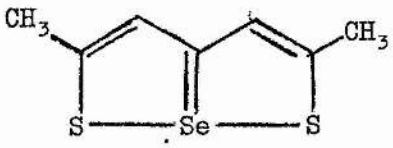
of the $C(CH_3)_2$ group about a mean position. At -60^{o} some broadening of the signals, especially that due to the methyl groups, was observed. The structure of compound (CV d) has recently been investigated by X-ray crystallography,[97] and the details are shown in fig. 19. A comparison of the bond lengths with the sum of the covalent radii of the appropriate atoms (table 1) indicates strong electronic interactions. Thus, the almost equivalent oxygen-selenium bonds are long compared to the covalent bond distance (1.83 Å) and the carbon-selenium bond (1.802 Å) has 70% double bond character when compared to the sum of the covalent single and double bond radii for carbon and selenium (table 1). The nitrogen-oxygen distances (1.346 and 1.337 Å) are similar to that (1.311 Å) found in the nitroso compound (fig. 16). The spectroscopic and crystallographic data is entirely consistent with the formulation of these compounds as bicyclic systems (CV) having partial oxygen-selenium bonds, not with their formulation as monocyclic systems (CI) as first proposed by King and Felton.

(7) Selenium Analogues of 6a-Thiathiophthenes.

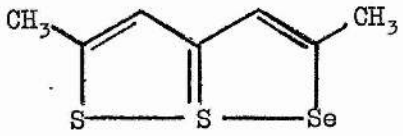
Traverso has described a synthesis (scheme 2) of the thiathiophthene analogue (CX) containing two selenium atoms.[100] Treatment of the pyrilium perchlorate (CVI) with sodium selenide gave the pyran selenoketone (CVII) in good yield. The selenoketone was ring opened with selenide and on careful acidification afforded compound (CVIII) which was formulated as the isomer (CXI) by Traverso. Aerial oxidation of compound (CVIII) gave the ketone (CIX) which, on treatment with phosphorus pentasulphide, gave the 6a-thiathiophthene analogue (CX), also obtained by direct



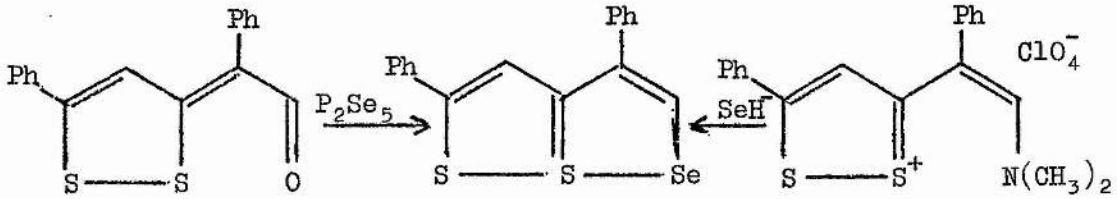
CXI



CXII



CXIII



CXV CXIV CXVI

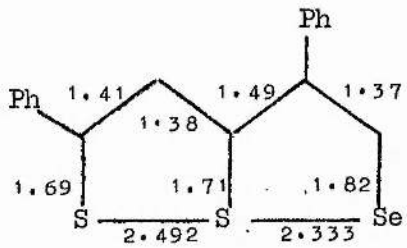


Fig. 20

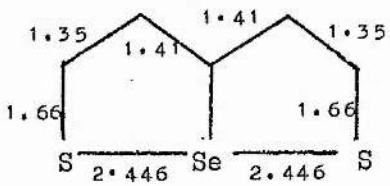
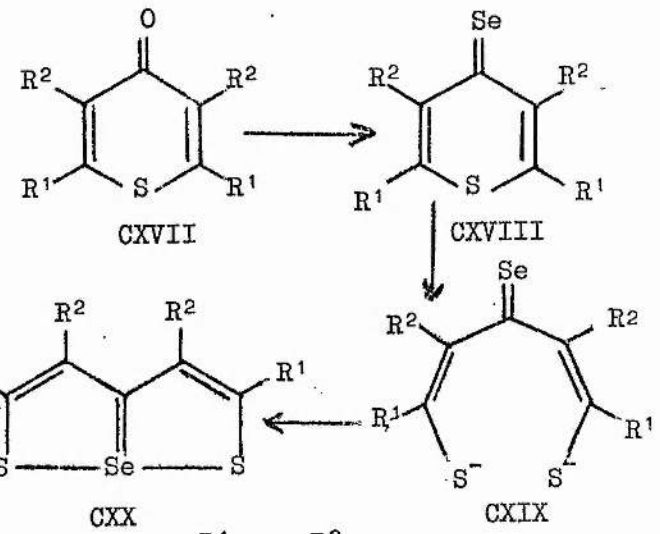


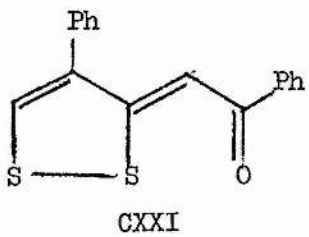
Fig. 21



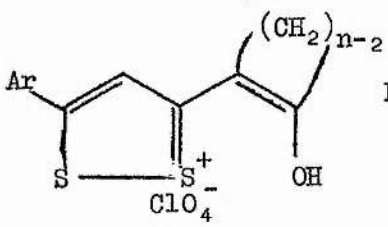
CXVII CXVIII CXIX CXX

	R^1	R^2
a)	H	H
b)	Ph	H
c)	H	CH_3

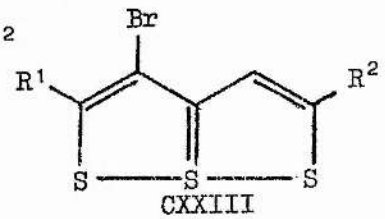
Scheme 3



CXXI



CXXII



CXXIII

	R^1	R^2
a)	CH_3	CH_3
b)	Ph	Ph
c)	CH_3	Ph
d)	SCH_3	Ph

treatment of compound (CVIII) with phosphorus pentasulphide. In a later paper,[58] the product obtained by heating the ketone (CIX) with phosphorus pentasulphide is formulated as the mono-selenium analogue (CXII) which was purified by repeated recrystallisation from toluene. It is probable that this reaction leads to a mixture of the two analogues (CX) and (CXII) which could possibly be separated by fractional recrystallisation. Pietra, Garbuglio and Mammi report[55] the isolation of the mono-selenium analogue (CXIII) from the reaction of the ketone (CIX) with phosphorus pentasulphide. The infra-red spectrum suggests the unsymmetrical structure (CXIII) rather than the symmetrical analogue (CXII) although it is difficult to see how the central selenium atom could be replaced by sulphur in this reaction.

The 2,4-diphenyl selenium analogue (CXIV) has been synthesised by two separate routes, from the corresponding 3-acylmethylene-3H-1,2-dithiole (CXV) by reaction with phosphorus pentaselenide,[67] and from the Vilsmeier salt (CXVI) by reaction with aqueous sodium hydrogen selenide.[24] Bond distances[67] for this analogue are shown in fig. 20. The sulphur-sulphur distance (2.492 Å) is almost identical to that (2.499 Å) found in the 6a-thiathiophthene (fig. 6). The sulphur-selenium distance (2.333 Å) is greater than the sum of the covalent radii but much shorter than the sum of the van der Waals radii for sulphur and selenium (table 1). If the difference in covalent radii between sulphur and selenium (0.12 Å) is subtracted from the found sulphur-selenium distance, the value 2.21 Å is obtained which is only 0.01 Å less than that actually found in the corresponding 6a-thiathiophthene (fig. 6).[98]

This result indicates that incorporation of selenium into the 6a-thiathiophthene system causes little, if any, change in the nature of the bonding.

Reid has synthesised[99] three symmetrical 6a-selenathiophthenes (CXX) (Scheme 3) by an elegant modification of the synthesis of the parent 6a-thiathiophthene.[27,28] The selenoketones (CXVIII) were obtained by treatment of the corresponding ketones (CXVII) in dimethylformamide with phosphoryl chloride, and of the resulting solutions with aqueous potassium selenosulphate. The unstable selenoketones (CXVIII) were ring opened by sodium sulphide giving solutions containing the dianions (CXIX) and/or related species. Intramolecular oxidative coupling of the dianions (CXIX) in situ by aqueous potassium ferricyanide gave the 6a-selenathiophthenes (CXX a-c). The symmetrical patterns of the N.M.R. spectra of the 6a-selenathiophthenes (CXX) in a variety of solvents show magnetic equivalence of ring protons or identical substituents at the pairs of sites C-2, C-5 and C-3, C-4. This demonstrates that these compounds in solution possess real or time-averaged C_{2V} symmetry. A structure study of the parent 6a-selenathiophthene reveals[156] that the equivalent sulphur-selenium bonds (2.446 Å) (fig. 21) are 10.1% longer than the sum of the covalent radii of sulphur and selenium (2.21 Å) (table 1). The length of the carbon-sulphur bonds (1.66 Å) agrees with the length of the terminal carbon-sulphur bonds (1.667 Å) in the parent 6a-thiathiophthene (fig. 2) and the lengths of the central and terminal carbon-carbon bonds in the two structures (figs. 2 and 21) agree closely.

In conclusion, there is no evidence at present to suggest a rapid

valence isomerisation between two monocyclic structures in the case of 6a-thiathiophthenes, selenium analogues of 6a-thiathiophthenes, isothiazolo [5,1-e] isothiazoles, aza-analogues of 6a-thiathiophthenes, or [1,2,5] oxaselenazolo [2,3-b][1,2,5] oxaselenazoles-7-Se^{IV}, and these compounds are all best described by a bicyclic formulation. The 3-acylmethylene-3H-1,2-dithioles, nitroso thiathiophthenes and nitrogen analogues of 6a-thiathiophthenes exhibit characteristics of sulphur-oxygen or sulphur-nitrogen bonding and therefore can be represented as bicyclic systems also. The nitro thiathiophthenes, on the other hand, show no characteristics of sulphur-oxygen bonding and consequently must be formulated as monocyclic compounds.

Chapter VI

Reactivity of 6a-Thiathiophthenes

(1) Carbonyl Reactions.

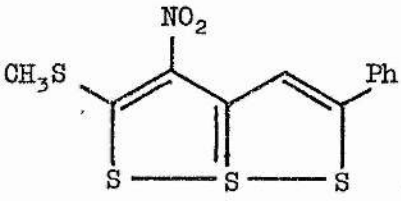
3-Acylmethylene-3H-1,2-dithioles, with a few exceptions e.g. (CXX1), undergo the usual carbonyl-type reactions, forming 2,4-dinitrophenylhydrazones[44,101] and aldimines.[82] 6a-Thiathiophthenes are more inert[44] under the same conditions, thus confirming the interaction of the three sulphur atoms in the 6a-thiathiophthene system, since one would expect a thioaldehyde structure to be more reactive than the corresponding aldehyde.

6a-Thiathiophthenes show typical thione properties in their reactions with mercury (II) compounds, forming salts with mercury(II)chloride.[3] The reaction of 6a-thiathiophthenes with mercury(II)acetate leads to replacement of one atom of sulphur by oxygen. This reaction is highly specific,[101] the sulphur atom adjacent to an unsubstituted carbon atom being replaced.

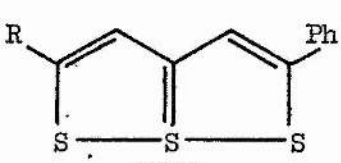
The ketones (XLVIII) form stable perchlorates (CXXII)[46] but no reaction with alkylating agents has been described. Unsymmetrical 6a-thiathiophthenes (LXXVI) are methylated by methyl iodide forming the iodides (LXXVII).[82] The iodides when treated with primary amines give aldimines (LXXVIII), also obtained directly from the 3-acylmethylene-3H-1,2-dithioles (LXXIX) by treatment with primary amines.

(2) Substitution Reactions.

2,5-dimethyl- and 2,5-diphenyl-6a-thiathiophthene have been brominated giving the monobromo derivatives (CXXIII a and b).[102]



CXXIV



CXXV

a) R = CH_3S
b) R = CH_3CH_2O
c) R = R^1NH

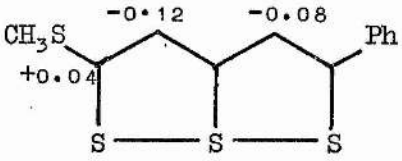
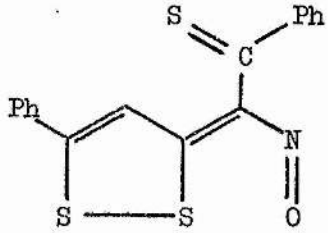
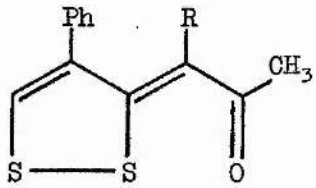


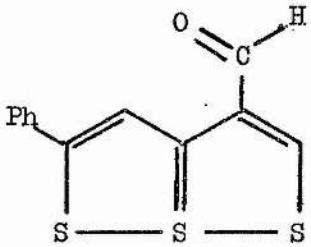
Fig. 22



CXXVI

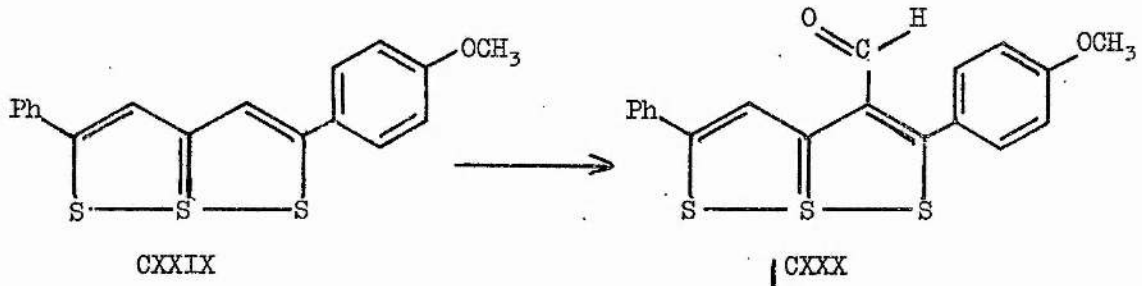


CXXVII



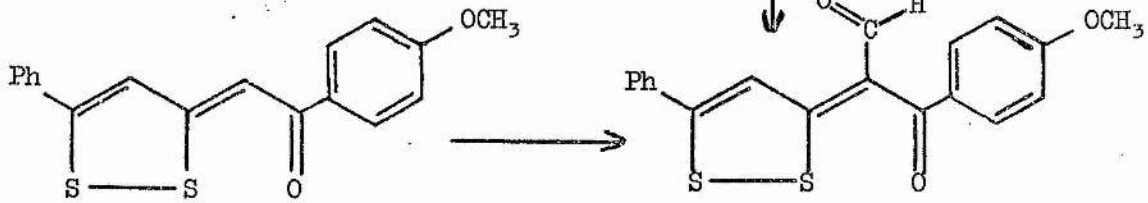
CXXVIII

a) R = H
b) R = Cl



CXXIX

CXXX



CXXXII

CXXXI

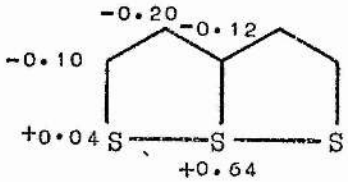
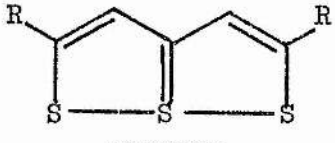
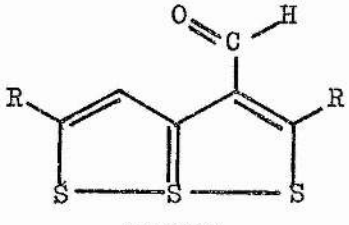


Fig. 23



CXXXIII

a) R = H
b) R = D



CXXXIV

a) R = H
b) R = D

Bromination of 2-methyl-5-phenyl- and 2-methylthio-5-phenyl-6a-thiathiophthene takes place in the 3-position in agreement with the calculated charge densities for these compounds, giving the products (CXXIII c and d). Similarly, nitration of 2-methylthio-5-phenyl-6a-thiathiophthene gives the 3-nitro derivative (CXXIV).[88] The methylthio group in 2-methylthio-5-phenyl-6a-thiathiophthene (CXXV a) is slowly replaced by nucleophiles. Thus, reaction with sodium ethoxide affords 2-ethoxy-5-phenyl-6a-thiathiophthene (CXXV b) and reaction with primary aliphatic amines gives 2-alkylamino-derivatives (CXXV c). Nitrosation of these compounds has already been discussed in chapter V part (5). 2-Methylthio-5-phenyl-6a-thiathiophthene (CXXV a) is attacked at the 3-position by electrophiles and at the 2-position by nucleophiles (with displacement of the methylthio group) in agreement with its calculated charge densities[88] (fig. 22). Formation of the nitroso-ketone (XCV) from the 6a-thiathiophthene (XCIV) by the action of nitrous acid probably involves electrophilic attack at the 3-position, followed by rearrangement to the geometrical isomer (CXXVI) and subsequent hydrolysis of the thiobenzoyl group.[90] Attempts to chlorinate 2-methyl-4-phenyl-6a-thiathiophthene were unsuccessful, but its oxygen analogue (CXXVII a) was chlorinated giving the compound (CXXVII b) which failed to react with phosphorus pentasulphide.[73]

Formylation of 2-phenyl-6a-thiathiophthene using dimethylthioformamide affords the 4-formyl derivative (CXXVIII), its structure being determined from its N.M.R. spectrum.[25] Symmetrical 2,5-diaryl-6a-thiathiophthenes have been formylated using dimethylformamide,[103] while formylation[104] of the unsymmetrical 6a-thiathiophthene (CXXIX) gave only one aldehyde (CXXX).

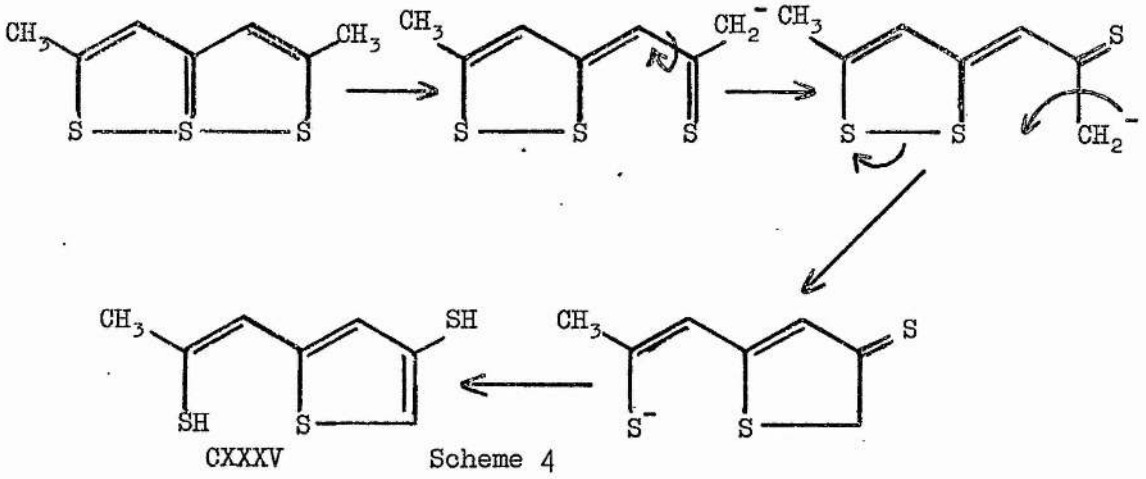
This structure was confirmed by peracetic acid oxidation to the dicarbonyl compound (CXXXI) which was also obtained by independant synthesis[104] and by formylation of the 3-acylmethylene-3H-1,2-dithiole (CXXXII).[105] Formylation of the parent 6a-thiathiophthene (CXXXIII a) occurs at the 3-position[106] giving the 3-formyl derivative (CXXXIV a) in accord with the net charge densities (fig. 23) calculated by Giacometti and Rigatti.[59] The position of formylation has been unambiguously determined by formylation of 2,5-dideuterio-6a-thiathiophthene[114] (CXXXIII b) to give 3-formyl-2,5-dideuterio-6a-thiathiophthene (CXXXIV b). Similar results were also obtained for formylation of 2-t-butyl-6a-thiathiophthene and its 5-deuterio derivative,[114] formylation occurring in the 4-position.

The electrophilic substitution reactions of 6a-thiathiophthenes, described above, demonstrate the aromatic character of the system.

(3) Side Chain Reactivity.

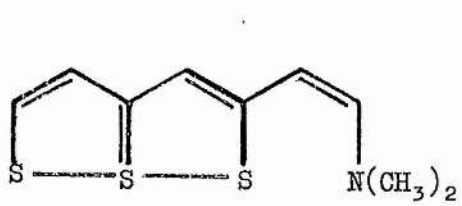
A methyl(ene) group in the 2-position of the 6a-thiathiophthene ring is reactive.[2,106] Action of alkali on 2,5-dimethyl-6a-thiathiophthene gives an unstable product eventually formulated[107,108] as the dimercapto-thiophene derivative (CXXXV), probably formed by the mechanism shown in scheme 4.[109] Stavaux and Lozac'h have condensed a number of 2-methyl- and 2-methylene-6a-thiathiophthenes with aromatic aldehydes[47] and carbon disulphide.[109] 3-Methyl-2,5-diphenyl-6a-thiathiophthene is unreactive. An attempted formylation[15] of 2-methyl-6a-thiathiophthene using dimethylthioformamide and phosphoryl chloride gave the enamine (CXXXVI).

The 2-amino-6a-thiathiophthene (CXXXVII) and the corresponding

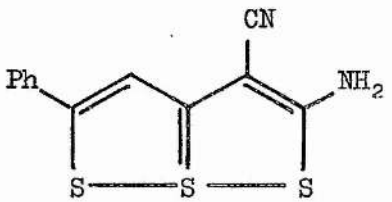


CXXXV

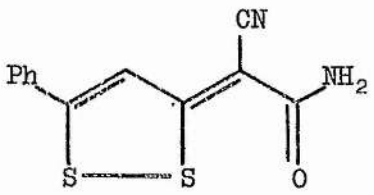
Scheme 4



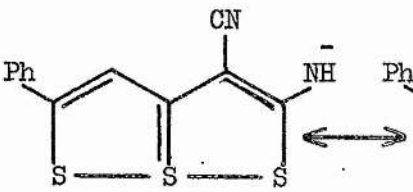
CXXXVI



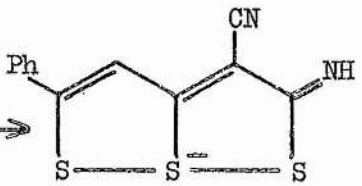
CXXXVII



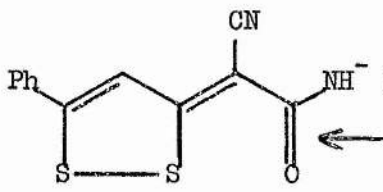
CXXXVIII



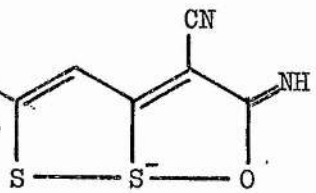
CXXXIX a



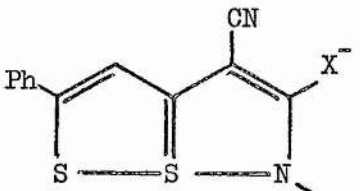
CXXXIX b



CXL a



CXL b



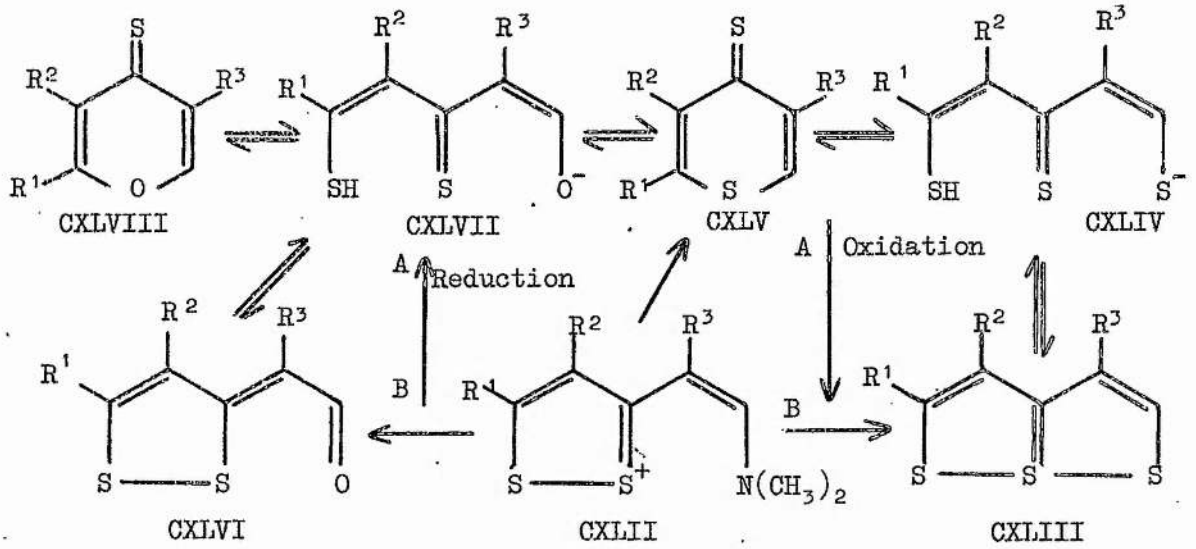
CXLI

a) X = S
b) X = O

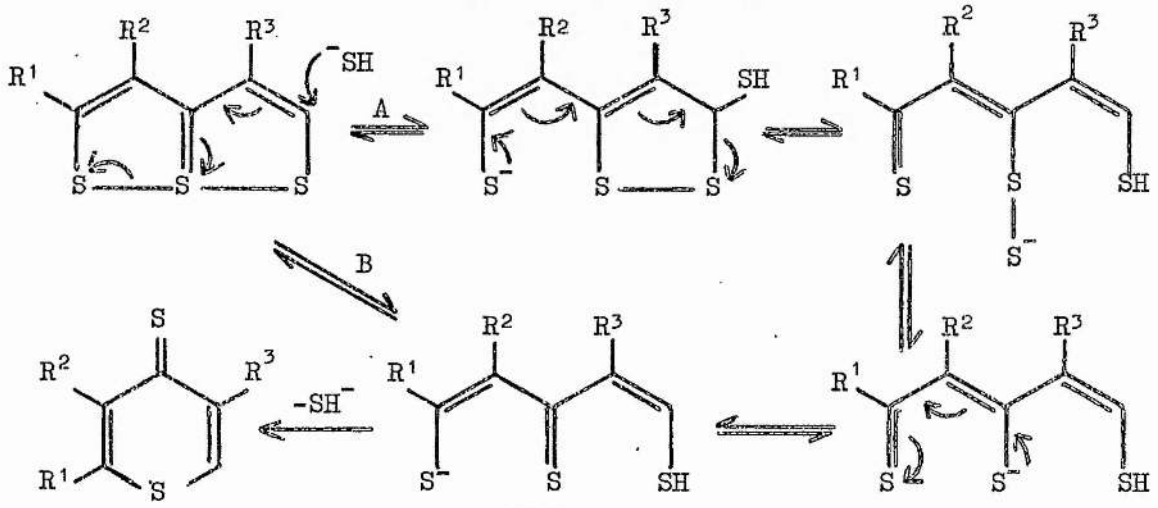
amide (CXXXVIII) are acidic and very stable to alkali. The U.V. spectra of these two compounds, although different in neutral solution, are almost identical in alkaline solution.[73] Klingsberg has suggested the possible resonance stabilised structures (CXXXIX a ⟷ CXXXIX b) and (CXL a ⟷ CXL b) to explain this,[73] but a more plausible explanation has been proposed by Beer[14] who has suggested that the anions (CXXXIX a) and (CXL a) contain the same system (CXLI a and b). Recent X-ray analysis of the nitrogen analogue (LXXXV, fig. 15) showing partial sulphur-nitrogen bonding[84] gives weight to this theory.

(4) Rearrangement Reactions.

Reaction of the Vilsmeier salt (CXLII a) with aqueous sodium hydrogen sulphide gave, in addition to the expected 2-methyl-6a-thiathiophthene (CXLIII a), the thiopyran thione (CXLV a).[24] A similar solvolysis of the Vilsmeier salt (CXLII b) resulted exclusively in formation of the thiopyran thione (CXLVb).[15] It has been established[29] that 6a-thiathiophthenes (CXLIII) are rearranged by sodium hydrogen sulphide or more completely by sodium sulphide to the thiopyran thiones (CXLV). At room temperature the rates of formation and decomposition of the 6a-thiathiophthenes are sufficiently different in most cases to allow the 6a-thiathiophthenes to be isolated in good yield from the Vilsmeier salts.[24] Thiopyran thiones (CXLV) are also formed by reaction of the Vilsmeier salts (CXLII)[15] and the 3-acylmethylene-3H-1,2-dithioles (CXLVI)[4,6,15] with sodium sulphide at higher temperatures. The reverse sequence, ring opening of the thiopyran thiones (CXLV) by

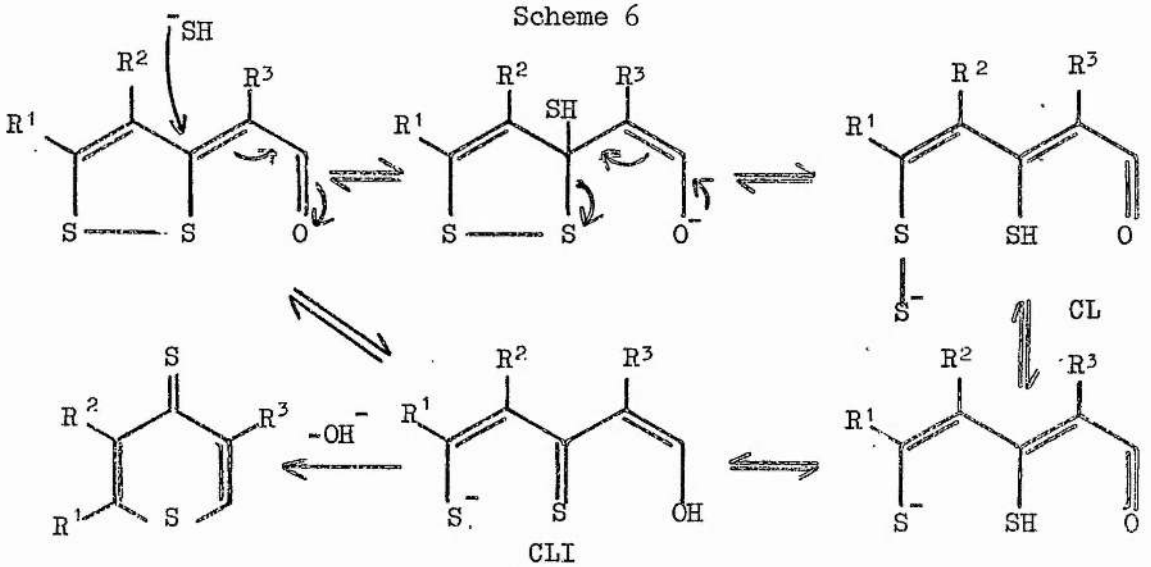


Scheme 5 a) $R^1=CH_3$, $R^2=R^3=H$
b) $R^1=H$, $R^2=R^3=Ph$



CXLIX

Scheme 6



CLI

Scheme 7

hydroxide or sulphide giving anions of type (CXLVII) and (CXLIV) respectively, and their intramolecular oxidation to 3-acylmethylene-3H-1,2-dithioles (CXLVI)[28] and 6a-thiathiophthenes (CXLIII)[27,28] has also been studied. Traverso has found that pyran thiones (CXLVIII), when treated with alkali metal sulphide or hydrosulphide, form thiopyran thiones (CXLV) and 3-acylmethylene-3H-1,2-dithioles (CXLVI),[3-6] the latter presumably being formed by atmospheric oxidation of the intermediate anion (CXLVII). This is a unique series of rearrangement reactions (scheme 5) where changes between levels A and B of the diagram involve an oxidation (A ⟶ B) or a reduction (B ⟶ A).

The rearrangement of 6a-thiathiophthenes to 4H-thiopyran-4-thiones (scheme 6) may proceed either by nucleophilic attack at the 2-position leading (route A) to the anion (CXLIX) which then cyclises, or by reductive cleavage of the sulphur-sulphur bond giving (route B) the same anion (CXLIX) directly.[29] The mechanism involving nucleophilic attack at the 2-position is more favoured by Dingwall and Reid for several reasons.[15,29] 2-Phenyl- and 2,4-diphenyl-6a-thiathiophthenes were also rearranged by aqueous hydroxide to give the corresponding 4H-thiopyran-4-thiones as major products. Since the hydroxide anion has no reducing power it is difficult to envisage any other mechanism other than one involving nucleophilic attack. It does not necessarily follow, however, that since reaction with hydroxide involves a nucleophilic attack, then rearrangement with sulphide or hydrosulphide must involve a nucleophilic attack also. Solvent effects appear to favour an initial nucleophilic attack.[15] In particular, 3,4-diphenyl-6a-thiathiophthene gives a 99% yield of 3,5-diphenyl-4H-thiopyran-4-thione in

dimethylformamide when reacted with aqueous hydrosulphide. When the reaction is carried out in methanol, the yield falls to only 20%. It seems unlikely that a change in solvent should have such a drastic effect on the reducing power of the hydrosulphide anion. 2,5-Diphenyl-6a-thiathiophthene gives only an 8% yield of 2,6-diphenyl-4H-thiopyran-4-thione[15] under conditions where 6a-thiathiophthenes unsubstituted in the 5-position rearrange giving 70-80% yields of the corresponding 4H-thiopyran-4-thiones.[29] This result, as well as the electronic effects of alkyl groups in substituted 6a-thiathiophthenes,[29] favours a mechanism involving nucleophilic attack. In the case of 2,5-diphenyl-6a-thiathiophthene both the 2- and 5-positions are effectively blocked against nucleophilic attack, whereas 3,4-diphenyl-6a-thiathiophthene, with no substituents on the 2- and 5-positions rearranges almost quantitatively.

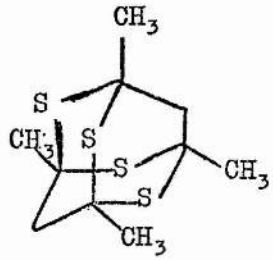
Traverso[4,6] proposed that the initial step in the rearrangement of 3-acylmethylene-3H-1,2-dithioles to give 4H-thiopyran-4-thiones involved a reductive cleavage of the sulphur-sulphur bond giving the anion (CL1) (Scheme 7) which then eliminated hydroxide ion on cyclisation. The intermediate anion (CL1) could also be formed by disproportionation of the intermediate (CL) arising from nucleophilic ring opening of the 3-acylmethylene-3H-1,2-dithiole by attack at the 3-position of the ring.[15]

Chapter VII

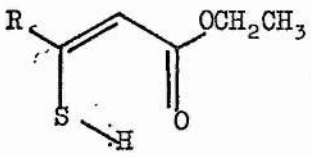
Thio- and Seleno-Derivatives of β-Diketones and their Transition Metal Chelates.

Mono- and polynuclear complexes containing Fe-S_n cores (n = 4,5 or 6) are currently commanding much attention because of their frequently unusual electronic and structural properties and their possible, although as yet unestablished, relevance to the iron-sulphur coordination units in nonheme iron proteins. The possibility also exists of using transition metal chelates as templates for further reactions on the ligand, particularly in cases where the ligand is unstable. Thio derivatives of β-diketones and their transition metal chelates are of particular interest since they are possible precursors of the 1,2-dithiolium cation and the 6a-thiathiophthene nucleus. A comprehensive review of the metal complexes of ligands containing oxygen, sulphur, selenium and tellurium has been written by Livingstone.[133]

The first recorded attempt to synthesise a thio derivative of a β-diketone was made by Fromm and Ziersch,[123] who isolated the dimer (CLII) from reaction of acetylacetone with hydrogen sulphide in alcohol using hydrogen chloride as catalyst. Ethyl thioacetoacetate (CLIII a) was prepared by Mitra,[124] and Reyes and Silverstein[125] synthesised ethyl thiobenzoylacetate (CLIII b) by a modification of Mitra's synthesis, which involved passing hydrogen sulphide into a solution of the β-diketone in ethanol saturated with hydrogen chloride. Livingstone and co-workers[126,127] synthesised a number of monothio-β-diketones (CLIV) by a similar method. The experimental conditions, such as temperature of reaction, concentration

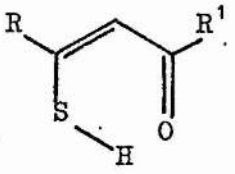


CLII



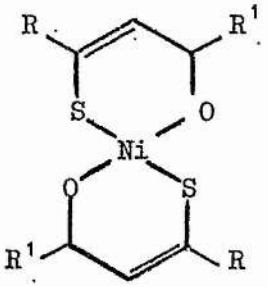
CLIII

a) R = CH_3
b) R = Ph

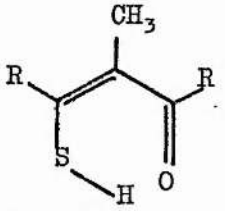


CLIV

R=CH_3; R^1=CH_3, Ph, OCH_2CH_3
R=Ph; R^1=Ph, OCH_2CH_3
R=2-thienyl, R^1=CF_3
R=R^1=$C(CH_3)_3$

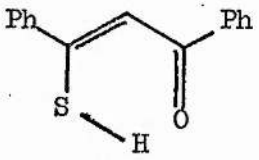


CLV

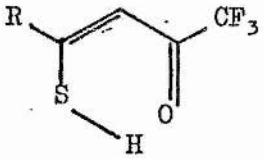


CLVI

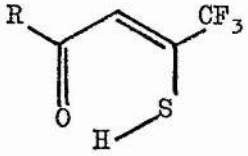
a) R=CH_3
b) R=Ph



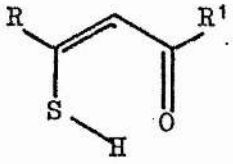
CLVII



CLVIII

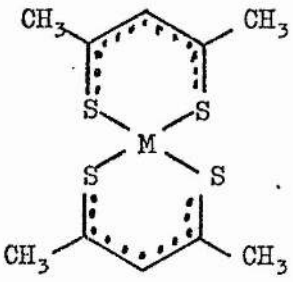


CLIX



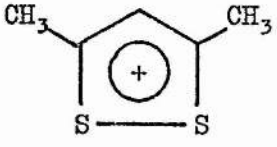
CLX

R=Ph, p-$CH_3C_6H_4$,
p-$CH_3OC_6H_4$, p-BrC_6H_4,
2-thienyl, 2-furyl, R^1=CF_3
R=Ph, R^1=Ph, OCH_2CH_3

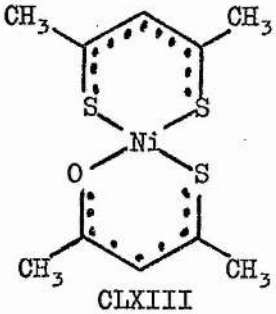


CLXI

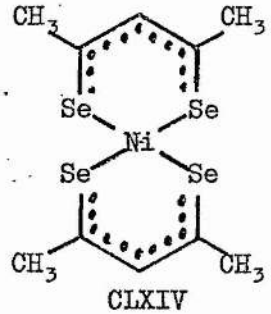
M=CO, Ni, Pd, Pt



CLXII



CLXIII



CLXIV

of β-diketone, and the time for which hydrogen sulphide and hydrogen chloride were passed through the solution, are very critical. Low concentrations of the β-diketone were used to avoid polymerisation giving products such as the tetrathiaadamantane (CLII). The mass, I.R. and N.M.R. spectra confirm that the products (CLIV) are entirely in the ene-thiole structure.

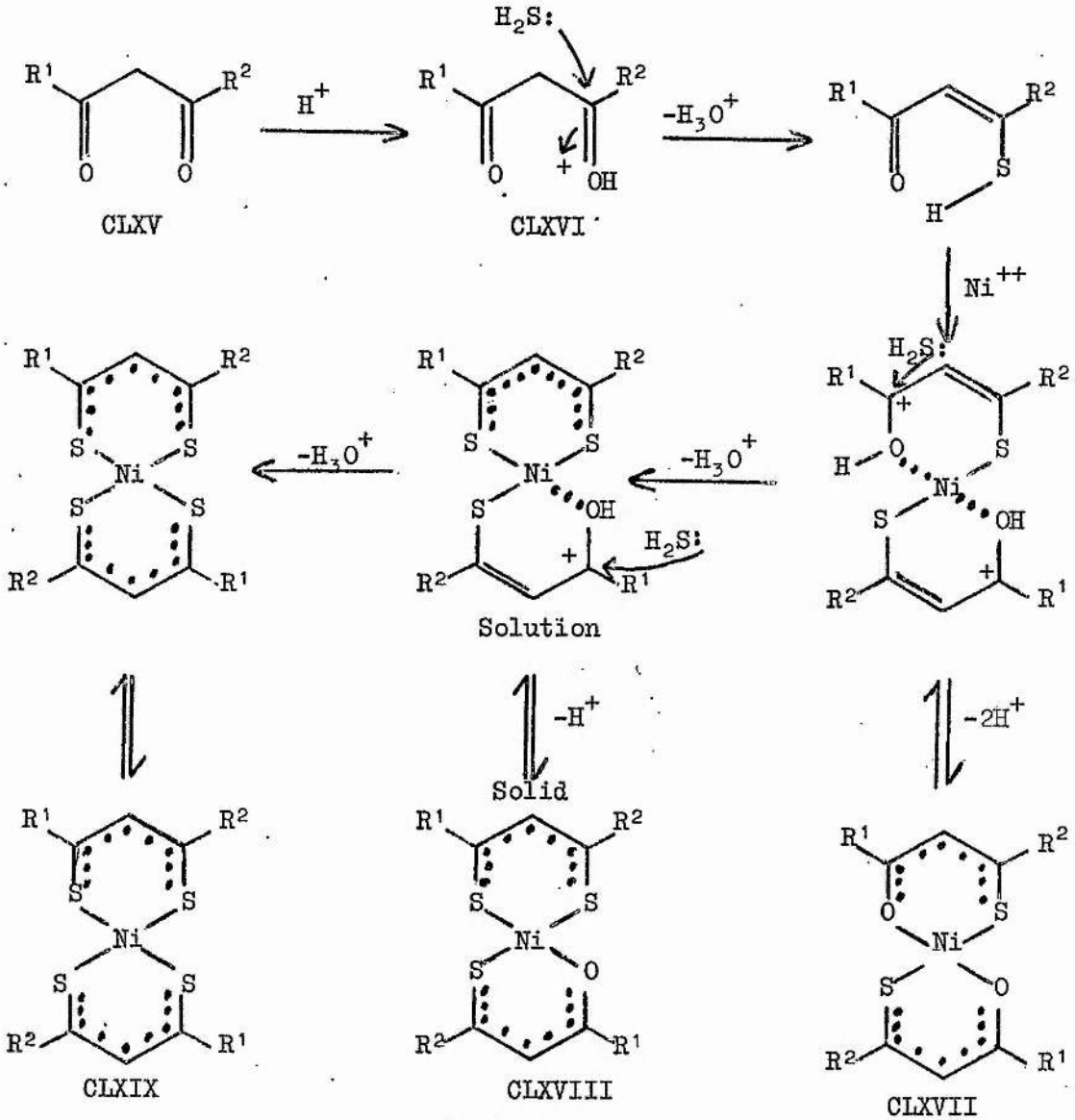
The monothio-β-diketones (CLIV) reacted with nickel acetate in alcohol solution giving the nickel chelates (CLV)[127] which were considered to have the square-planar trans structure (CLV) because of their diamagnetism and solubility in non-polar organic solvents. The replacement of one oxygen atom in β-diketones by sulphur thus causes a change in bond-type of the respective nickel (II) chelates from spin-free to spin-paired.[127] The conversion of two α-C-methyl-β-diketones to the monothio-β-diketones (CLVI) was found to be more difficult.[128] Nickel (II) complexes of both ligands (CLVI a and b) and the cobalt (III) complex of the ligand (CLVI a) were synthesised but the cobalt (III) complex of (CLVI b) and other metal complexes of both ligands could not be isolated, presumably because of strong steric clashing of the α-methyl group with the terminal phenyl or methyl groups. Bis and tris complexes of 3-mercapto-1,3-diphenyl-prop-2-ene-1-one (CLVII) with a large number of transition metals have been reported.[130] The method of synthesis involved the addition of aqueous or ethanolic solutions of a transition metal salt to solutions of the ligand in acetone or alcohol. A number of metal chelates of the trifluoromethyl ligand (CLVIII) have been prepared[131,132,134] and the ligands are all assumed to have structure (CLVIII) rather than the isomeric structure (CLIX) since mass

spectrometry has established[127] that when R = phenyl or thienyl, substitution of one oxygen by sulphur takes place at the carbonyl group furthest away from the trifluoromethyl group.

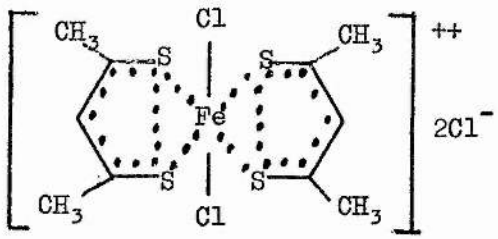
The magnetic susceptibilities of the iron (III) chelates with the ligands (CLX) have been investigated over a temperature range.[136] The moments of the complexes vary between 2.31 and 5.61 B.M. at room temperature and are temperature-dependent ranging from 1.86 to 4.07 B.M. at 80°K, depending on the nature of the substituents. This behaviour is postulated to be due to a thermal equilibrium between the nearly equi-energetic spin-paired and spin-free configurations of the iron atom, resulting from the approximately equal magnitudes of the ligand field and the pairing energy in these complexes. The ligand field and consequently the magnetic behaviour are sensitive to the nature of the substituents; electron-withdrawing groups appear to be the most effective in increasing the population of the spin-paired configuration. The electronic spectra of some metal chelates of monothio-β-diketones have been reported[135] but no generalisations can be made. The I.R. spectra of the monothio-β-diketones show no peak due to SH bending at ca. 2570 cm^{-1} indicating strong chelation of the thiol proton between the sulphur and oxygen atoms.[125-127,133] The I.R. spectra of the ligands, metal complexes and some adducts have been discussed in detail.[126-130,132-134]

Stewart and Martin reasoned that the isolation of the dimer (CLII) by Fromm and Ziersch[123] suggested the initial formation of dithioacetylacetone.[137] In the presence of the appropriate transition metal salt,

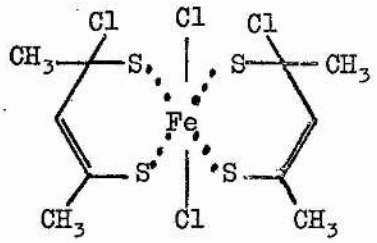
the reaction between acetylacetone and hydrogen sulphide in ethanolic hydrogen chloride afforded[137] the cobalt (II), nickel(II), palladium (II), and platinum (II) complexes with dithioacetylacetone. These complexes were stable, crystalline solids, soluble in organic solvents giving intensely coloured solutions. Magnetic susceptibility measurements showed that the cobalt (II) chelate is paramagnetic and the other chelates are diamagnetic thus favouring a square-planar structure (CLXI) later confirmed[138] by X-ray crystallography for the cobalt (II) and nickel (II) complexes. The cobalt (II) complex is completely coplanar and the bond distances are comparable with the values expected for a system where extensive delocalisation would be predicted. The N.M.R. spectrum of the nickel (II) chelate, showing two singlets in the ratio 6:1, indicated the symmetry of the molecule. Not surprisingly, the mass spectra of all the complexes show, as well as molecular ion peaks, an intense peak at m/e 131 attributed to the 3,5-dimethyl-1,2-dithiolium cation (CLXII). Several substituted dithio-β-diketone complexes of cobalt (II) and nickel (II) have been isolated by Japanese workers.[148] A series of nickel(II) complexes of acetylacetone has been synthesised where two, three and four oxygen atoms are replaced by sulphur[144,147] and the nickel (II) complexes of 1,1,1-trifluorodithioacetylacetone, dithiobenzoylacetone and diseleno-acetylacetone have been obtained[144] by a similar synthesis. All these nickel (II) complexes have square-planar monomeric structures, unlike the nickel (II) complex of acetylacetone which is trimeric. The I.R. spectra of the complexes have been discussed in detail.[144] The N.M.R. spectrum of nickel (dithioacetylacetone)(monothioacetylacetone) (CLXIII) shows four singlets in the ratio 1:1:3:9 as expected,[144,147] but the



Scheme 8



CLXX

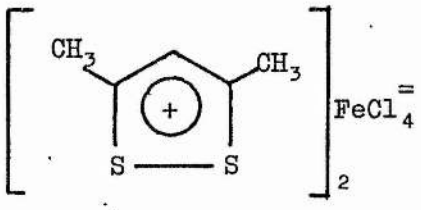


CLXXI

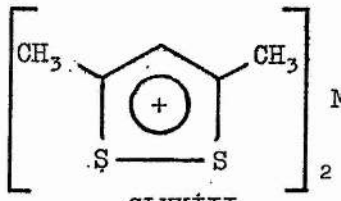
spectrum of nickel (diselenoacetylacetone) (CLXIV) could not be obtained because of the compound's insolubility.[144]

A mechanism has been proposed (scheme 8) for the formation of these square-planar metal complexes. In ethanolic hydrogen chloride, the diketone would exist almost entirely in the keto form (CLXV), and protonation of the oxygen atom, giving the ion (CLXVI) sensitises the carbon atom to nucleophilic attack by hydrogen sulphide. The isolation of bis(monothioacetylacetone) nickel (II) (CLXVII) and (dithioacetylacetone) (monothioacetylacetone) nickel (II) (CLXVIII) and their conversion[144] to bis (dithioacetylacetone) nickel (II) (CLXIX) confirms that coordinated monothioacetylacetone can react with hydrogen sulphide giving coordinated dithioacetylacetone without the free monomeric ligand being formed at any stage. The mechansim (scheme 8) agrees with the syntheses of unsymmetrically substituted monothio-β-diketones by Livingstone[126,127,131-4] who found that replacement of oxygen by sulphur occurred at the carbon atom furthest from the more electron withdrawing of the two substituents. Thus if R^1 is a more electron withdrawing group than R^2, then the oxygen atom adjacent to R^2 will be the more basic. Protonation of that oxygen atom and hence attack by hydrogen sulphide at the carbon bonded to R^2 results in replacement of the more basic oxygen atom, which is furthest from the more electron withdrawing group R^1.

When Martin's synthesis of bis(dithioacetylacetone) metal (II) complexes[137] was repeated in the presence of ferric ion as the transition metal, a violet crystalline product $Fe(C_5H_7S_2)_2Cl_4$ was obtained, the deep colour of which led Knauer[112] to suggest the presence of Fe-SS coordination in structures such as (CLXX) or (CLXXI) although it

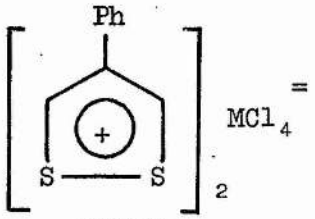


CLXXII



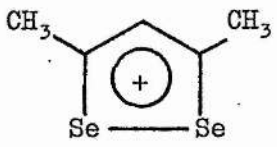
CLXXIII

M= Mn, Fe, Co, Ni
X= Cl, Br

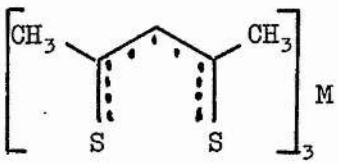


CLXXIV

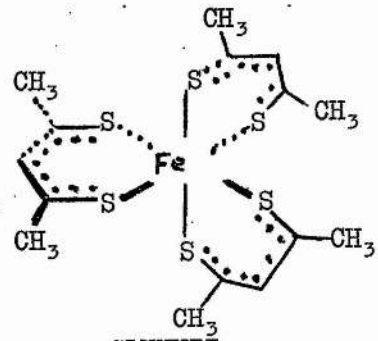
M= Fe, Co, Ni



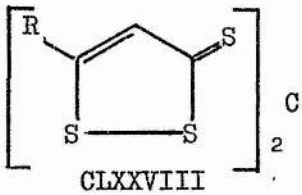
CLXXV



CLXXVI



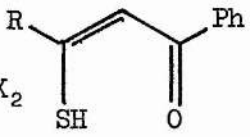
CLXXVII



CLXXVIII

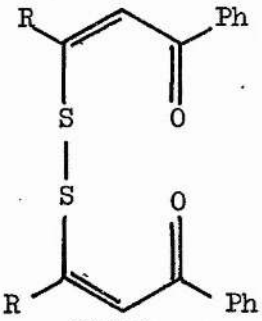
R=H, Ph, 2-thienyl
X=Cl, Br, I

CoX_2



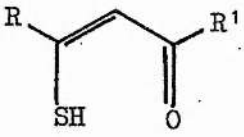
CLXXIX

a) $R=CH_3$
b) R=Ph



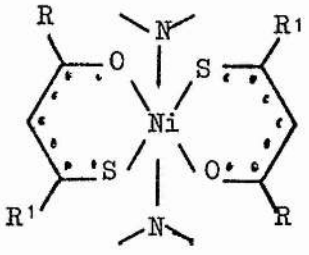
CLXXX

a) $R = CH_3$
b) R = Ph

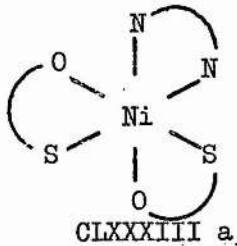


CLXXXI

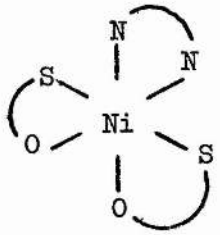
$R=CH_3$; $R^1=OCH_3$, OCH_2CH_3, CH_3
R=Ph; $R^1=OCH_2CH_3$, Ph
R=2-thienyl, $R^1=CF_3$
$R=R^1=(CH_3)_3C$



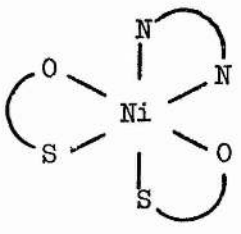
CLXXXII



CLXXXIII a



CLXXXIII b



CLXXXIII c

was shown that the colourless aqueous solution contained iron (II), chloride, and 3,5-dimethyl-1,2-dithiolium ions. Furuhashi synthesised[140] similar manganese (II) and mercury (II) complexes by the same method and on the evidence of the IR spectra of the manganese (II), mercury (II) and iron (II) complexes, assigned relative strengths to the proposed metal-sulphur bonds, in support of Knauer's suggestion. Similar iron (II) and cobalt (II) compounds $M(C_{15}H_{11}S_2)_2Cl_4$ were obtained with dibenzoylmethane as the β-diketone,[148] and with acetylacetone the complexes $M(C_5H_7S_2)_2Br_4$ were obtained[149] in ethanolic hydrogen bromide where the transition metal was manganese (II), iron (II), cobalt (II), copper (II), zinc (II) and cadmium (II).

The structure of the iron (II) compound of dithioacetylacetone $Fe(C_5H_7S_2)_2Cl_4$ was confirmed to be a tetrachloroferrate (II) salt (CLXXII) of the 3,5-dimethyl-1,2-dithiolium cation by its diffuse reflectance spectrum and magnetic studies which confirmed the existence of the tetrahedral tetrachloroferrate (II) anion.[141] The same conclusion was reached independantly from an X-ray crystal structure determination of the compound.[142] The close contact (3.33 Å) observed between the chlorine and sulphur atoms is significantly shorter than the sum of the van der Waals radii of sulphur and chlorine (3.65 Å) and implies that charge transfer is taking place from the strongly reducing tetrachloroferrate (II) anion to the delocalised 1,2-dithiolium cation, which explains the deep violet colour of the complex. The preparation of an extended series of similar tetrahalometallate (II) salts of the 3,5-dimethyl-1,2-dithiolium (CLXXIII) and 4-phenyl-1,2-dithiolium (CLXXIV) cations has been reported.[143] Two salts, the tetrachlorocobaltate (II) and the iodide,

of the previously unknown 3,5-dimethyl-1,2-diselenolium cation (CLXXV) were also synthesised. The electronic and Mössbauer spectra together with the temperature dependance of the magnetism of the compounds established their formulation as tetrahalometallate (II) salts. The close similarity of the I.R. spectra of the compounds (CLXXIII) and (CLXXIV) indicated isostructural series. The absence of systematic shifts in the spectra upon variation of the metal or replacement of chloride by bromide confirms there is no significant interaction of the metal ion with the organic moiety.

The tris (dithioacetylacetonato) metal (III) complexes (CLXXVI) where the transition metal is cobalt, rhodium or iridium[145] and iron, ruthenium, or osmium[113] have recently been synthesised. The rhodium and iridium complexes separate directly from solutions of the tervalent metal ion with acetylacetone in ethanolic hydrogen chloride saturated with hydrogen sulphide. Oxidation of bis(dithioacetylacetonato) cobalt (II) (CLXI, M = Co) with molecular oxygen in the presence of acetylacetone and hydrogen sulphide in ethanolic hydrogen chloride gave, in addition to the tris (dithioacetylacetonato) cobalt (III) complex (CLXXVI, M = Co), the bis(1,2-dithiolium) tetrachlorocobaltate (II) salt (CLXXIII, M = Co, X = Cl). The ruthenium and osmium complexes were prepared[113] by a similar method to the rhodium and iridium complexes,[145] starting from ruthenium trichloride and osmium tetroxide. Tris (dithioacetylacetone) iron (III) (CLXXVI, M = Fe) has also been synthesised by reduction of bis(3,5-dimethyl-1,2-dithiolium) tetrachloroferrate (II) (CLXXII) in aqueous acid with sodium borohydride or sodium dithionite.[112] The products obtained by dissolving iron(II) chloride with acetylacetone in

ethanolic hydrogen chloride and saturating the solution with hydrogen sulphide depend critically on the reaction conditions.[113] It was found that the dimer (CLII), bis (3,5-dimethyl-1,2-dithiolium) tetrachloroferrate (II) (CLXXII) and tris(dithioacetylacetonato) iron (III) (CLXXVI, M = Fe) could all separate consecutively or simultaneously from the reaction mixture. The cobalt, rhodium and iridium complexes (CLXXVI, M = Co, Rh and Ir) are diamagnetic and their mass spectra are all characterised by a strong peak at m/e 131 attributed to the 3,5-dimethyl-1,2-dithiolium cation.[145] The iron, ruthenium and osmium complexes (CLXXVI, M = Fe, Ru and Os) are paramagnetic, stable to air and moisture and moderately soluble in organic solvents giving intense brown solutions.[113] Again, the mass spectra of these three complexes shows the strongest peak corresponds to the 3,5-dimethyl-1,2-dithiolium cation (CLXII). An X-ray structural analysis of tris(dithioacetylacetonato) iron (III) shows an octahedral arrangement of the six sulphur atoms around the central iron atom (CLXXVII).[113]

Furuhashi[150] has reported the synthesis of complexes of rhodium (III) and platinum (II) with "trithiodiacetylacetone" and also claims the isolation of complexes of molecular formula $Co(C_7H_{10}SO_2)_2Cl_2$ and $Co(C_7H_{10}O_3)_2Cl_2$ which were obtained by grinding cobalt (II) chloride hexahydrate with 2,5-dimethyl-6a-thiathiophthene and diacetylacetone respectively. The author appears to be unaware of the current literature on 6a-thiathiophthene chemistry and states that the NMR. spectrum of "trithiodiacetylacetone" prepared by Arndt's synthesis[1] shows four singlets in the ratio 1:1:3:3.

Recently, Pettilon and Guerchais have synthesised complexes of cobalt (II) with 1,2-dithiole-3-thiones.[151] These complexes

(CLXXVIII) are soluble in organic solvents and have been shown to be covalent by conductivity measurements. On the basis of their electronic spectra and magnetic properties, a tetrahedral arrangement around the cobalt atom has been established. Interestingly, it has also been shown from a study of their IR. spectra that coordination between the cobalt atom and the organic moiety takes place through the thione group and not through the ring sulphur atoms.

Very few reactions of thio-derivatives of β-diketones and their transition metal complexes have been reported. Alcoholic solutions of the monothio-β-diketones (CLXXIX) are oxidised to the disulphides (CLXXX) when left standing for several weeks.[127] The iron (III) complex with the ligand (CLXXIX b) is also decomposed in aqueous alcohol yielding the disulphide (CLXXX b). Iodine effects this oxidation within a few seconds.[130] The nickel (II) chelates of the monothio-β-diketones (CLXXXI) form adducts with the nitrogenous bases pyridine, γ-picoline, 1,10-phenanthroline, 2-methyl-1,10-phenanthroline, 2,2'-bipyridyl and 2,2',2''-terpyridyl.[129] Trans octahedral structures (CLXXXII) were assumed for the pyridine and γ-picoline adducts whereas there are three possible structures (CLXXXIII a, b and c) for the adducts with 1,10-phenanthroline, 2-methyl-1,10-phenanthroline and 2,2'-bipyridyl. It has been found that the pyridine and γ-picoline adducts of the fluorinated monothio-β-diketones (CLVIII) are more stable than their unfluorinated adducts.[132] This is due to the strong electron withdrawing power of the trifluoromethyl group which weakens the nickel-oxygen and nickel-sulphur bonds. The electron demand of the nickel atom is thus increased, and so stronger bonds are formed with the nitrogen atoms of the ligands in the apical

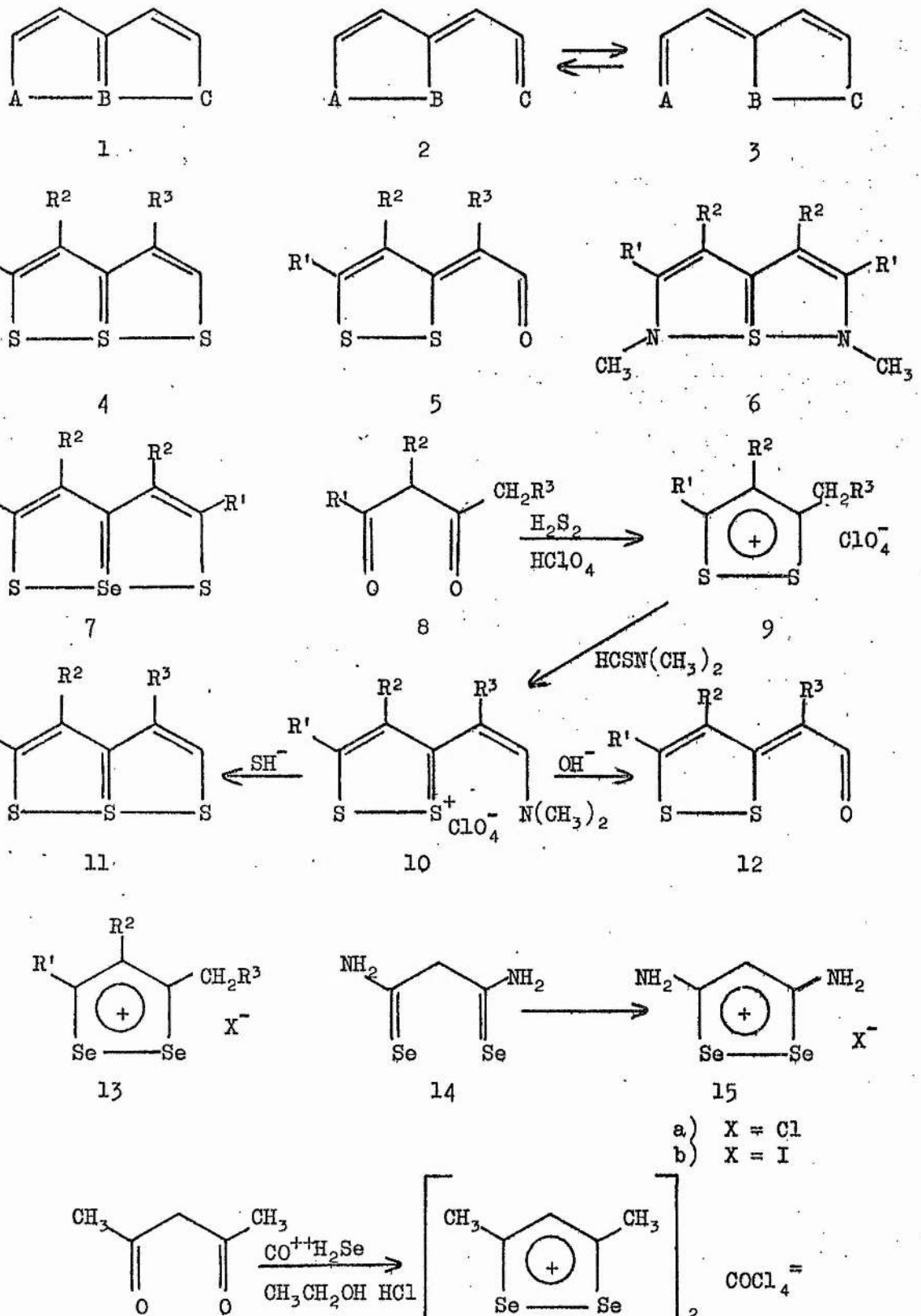
octahedral sites. The square planar complex (CLXI, M = Fe) forms a dicarbonyl adduct with carbon monoxide at room temperature and atmospheric pressure.[152] The I.R. spectrum of the adduct shows two carbonyl stretching bands at ca. 2000 cm^{-1} and a cis configuration is thus inferred. Reaction of the dicarbonyl adduct with pyridine results in the replacement of one carbonyl group by pyridine, whereas reaction with nitric oxide forms the adduct bis(dithioacetylacetonato)dinitrosyl iron (II) which is also formed directly from the square planar complex (CLXI, M = Fe) with nitric oxide.[152] Again a cis configuration is inferred from the I.R. spectrum. An adduct is also formed between bis(dithioacetylacetonato) iron (II) and oxygen but no structural details are given.

Collman[154] has reviewed the reactions of tris(acetylacetonato) metal (III) chelates. Those with chromium, cobalt and rhodium are so stable that the central hydrogen atom on the chelate ring can be substituted as in benzene. They can be halogenated with N-bromosuccinimide or iodine chloride, acylated with acetic anhydride and boron trifluoride, formylated with phosphoryl chloride and dimethylformamide, converted into thiocyanates with dithiocyanogen and into thioethers with sulphenyl chlorides. They can be chloromethylated with chloromethyl ether, and nitrated with copper nitrate in acetic anhydride. The nitro compound can be reduced to the amine; this gives a stable diazonium salt, which couples with β-naphthol, can be converted into the hydroxy compound by heating, is reduced by ethanol and can even be converted into the fluoro compound. The bond character of β-diketone metal chelates has been discussed[153] in great detail and a critical appraisal has been made

of whether it is justifiable to attribute any aromatic character to such molecules. Comparisons of the reactivity of β-diketone metal chelates with benzene have led to controversial conclusions concerning the bond character in metal chelates of acetylacetone.[153] At the present time it is impossible to elaborate on the bond character and aromaticity of dithio-β-diketone metal chelates since so little work has been carried out with these complexes.

PART TWO

DISCUSSION


A B C
1
2
3
R2 R3 R' S S S
4
5 O
6 N CH3
7 Se
8 CH2R3 H2S2 HClO4
9 ClO4-
HCSN(CH3)2
10 N(CH3)2
11 SH-
12 OH-
13 X-
14 NH2
15
a) X = Cl
b) X = I
CH3 CO++H2Se
CH3CH2OH HCl
COCl4=
16

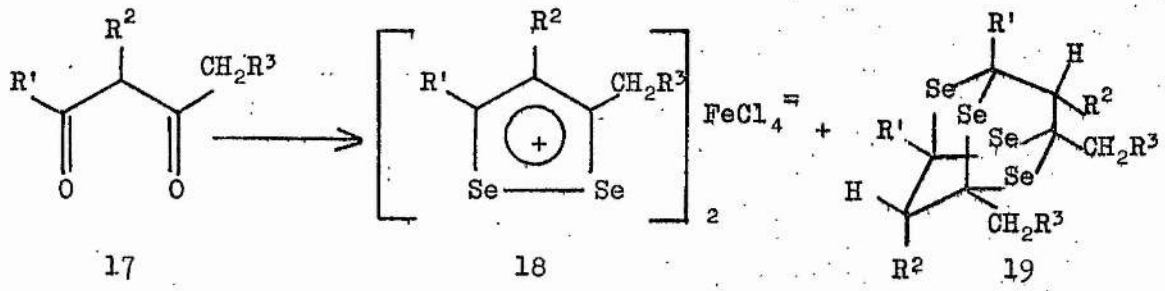
CHAPTER I

The Synthesis of Selenium Analogues of 6a-Thiathiophthenes and Related Compounds.

During the past four years, it has been one of the aims in these laboratories to synthesise analogues (1) of the 6a-thiathiophthene system where A and C are elements of Group 5 (N–R and P–R) or Group 6 (O, S, Se and Te) and B is an element theoretically capable of valence-shell expansion. The study of these compounds by spectroscopy and by X-ray crystallography will give evidence for the presence or absence of A–B or B–C covalent bonding, and hence on whether these compounds may be formulated as bicyclic systems (1) or by a system of interconverting valence isomers (2 ⟷ 3).

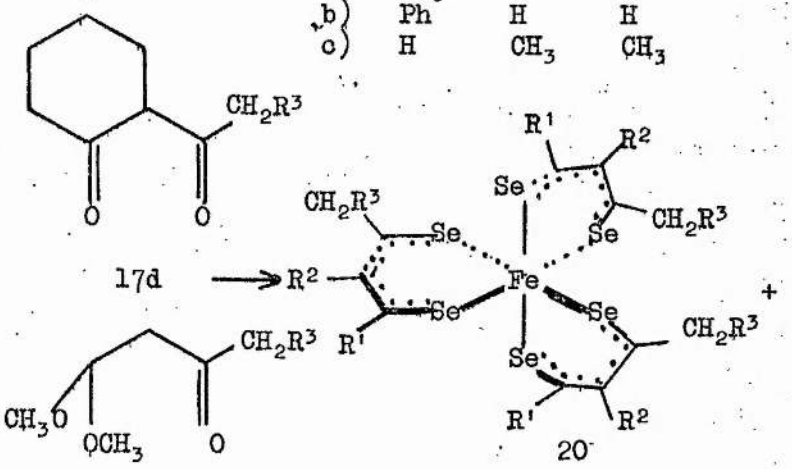
Theories of bonding in 6a- thiathiophthenes (4) and 3-acylmethylene-3H-1,2-dithioles (5) and their chemistry are now becoming well established.[32,46,52,61–63,139] Very recently, the isothiazolo [5,1-e] isothiazoles[18,86] (6) and the selenium analogues[99] (7) have been synthesised. These compounds, with the exception of the 3-acylmethylene-3H-1,2-dithioles (5), are best formulated as bicyclic systems. It was decided that a comprehensive study should be made of selenium analogues of 6a-thiathiophthenes with a view to studying the effect on the structure of replacing the three sulphur atoms in 6a-thiathiophthenes (4) by three selenium atoms and by combinations of oxygen, sulphur and selenium. A versatile synthesis of selenium analogues of 6a-thiathiophthenes was therefore sought.

The most versatile synthesis of 6a-thiathiophthenes (11) yet developed involves the formation[24] of a 3-methyl(ene)-1,2-dithiolium salt (9) by reaction of hydrogen disulphide with the corresponding 1,3-diketone (8), its condensation with dimethylthioformamide,[24,25] and solvolysis of the resulting Vilsmeier salt (10) with aqueous hydrosulphide.[24] Solvolysis of the salt (10) with aqueous hydroxide affords the 3-acylmethylene-3H-1,2-



17 18 19

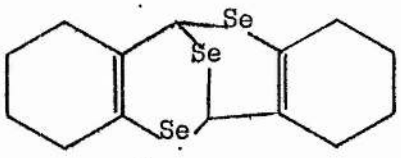
	R'	R^2	R^3
a)	CH_3	H	H
b)	Ph	H	H
c)	H	CH_3	CH_3



17d 20 19

17e

	R'	R^2	R^3
d)	H	$-CH_2CH_2CH_2-$	
e)	H	H	H



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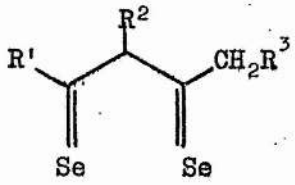

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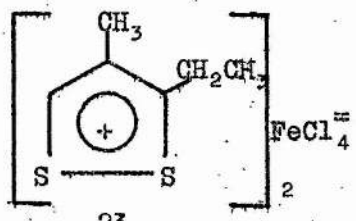

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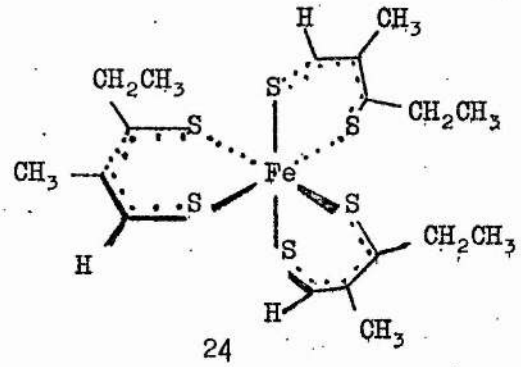


24

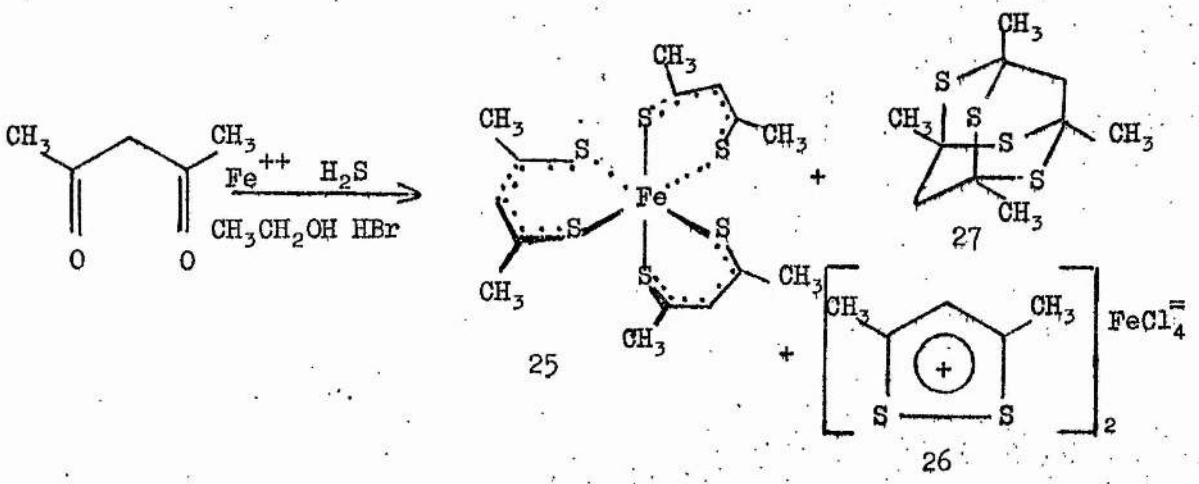
dithiole[24] (12). 3-Methyl(ene)-1,2-diselenolium salts (13) cannot be prepared by the same method as was used for the preparation of the 3-methyl(ene)-1,2-dithiolium salts (9) since hydrogen diselenide has never been prepared, presumably because of the weakness of the diselenide bond. Prior to this work, the salts of only two 1,2-diselenolium cations had been prepared. Jensen synthesised[157] 3,5-diamino-1,2-diselenolium chloride (15a) and iodide (15b) by oxidation of diselenomalonamide (14) with iron(III) chloride and iodine respectively. 3,5-Dimethyl-1,2-diselenolium tetrachlorocobaltate (II) (16) was prepared by Heath, Martin, and Stewart[143] by dissolving cobalt (II) carbonate and acetylacetone in ethanolic hydrogen chloride and passing hydrogen selenide through the solution.

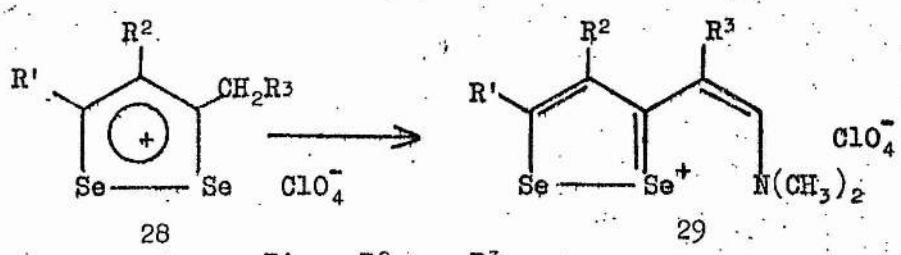
(1) Bis(1,2-Diselenolium) Tetrachloroferrates (II) (18).

The synthesis of 3,5-dimethyl-1,2-diselenolium tetrachlorocobaltate (II) (16) has now been modified by using iron (III) chloride and has been applied to four 1,3-diketones (17a-d) and 4,4-dimethoxy-butane-2-one (17e). Using acetylacetone (17a), benzoylacetone (17b), and 2-hydroxymethylene-pentane-3-one (17c), reaction with hydrogen selenide in ethanolic hydrogen chloride containing iron (III) chloride afforded the corresponding bis(1,2-diselenolium)tetrachloroferrates (II) (18a-c) and the corresponding 2,4,6,8-tetraselenaadamantanes (19a and c).

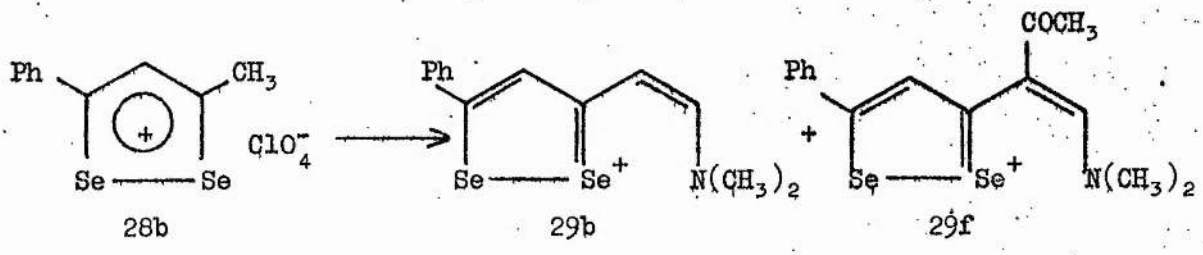
(2) Tris (1,3-Diselenato) Iron (III) Complexes (20).

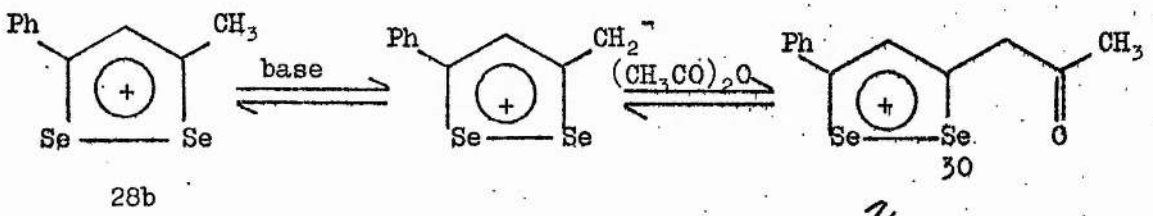
2-Hydroxymethylene cyclohexanone (17d) and 4,4-dimethoxy-butane-2-one (17e), when reacted under the same conditions as was used for the preparation of the bis (1,2-diselenolium) tetrachloroferrates (II) (18), unexpectedly gave tris(2-selenoformylcyclohexane-1-selenato) iron (III) (20d) and tris(3-selenobut-1-ene-1-selenato) iron (III) (20e). The 2,4,6,8-tetraselenaadamantanes (19d and e) were also isolated from the reaction mixtures and, using 2-hydroxymethylene cyclohexanone (17d), a further dimerisation product, 2,10,17-triselenatetracyclo[7,7,1,$0^{3,8}$

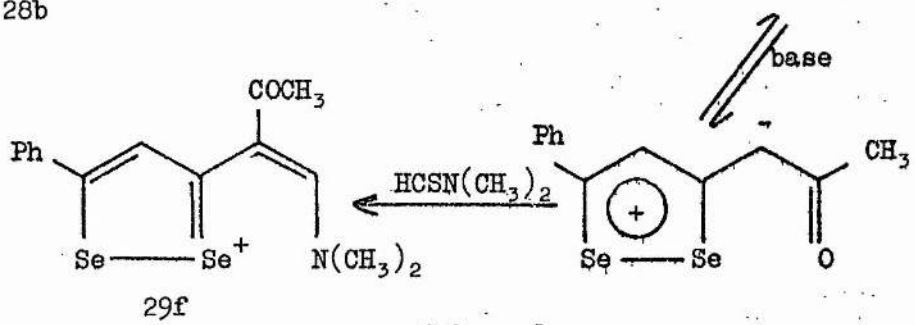




	R'	R^2	R^3
a)	CH_3	H	H
b)	Ph	H	H
c)	H	CH_3	CH_3







Scheme 1

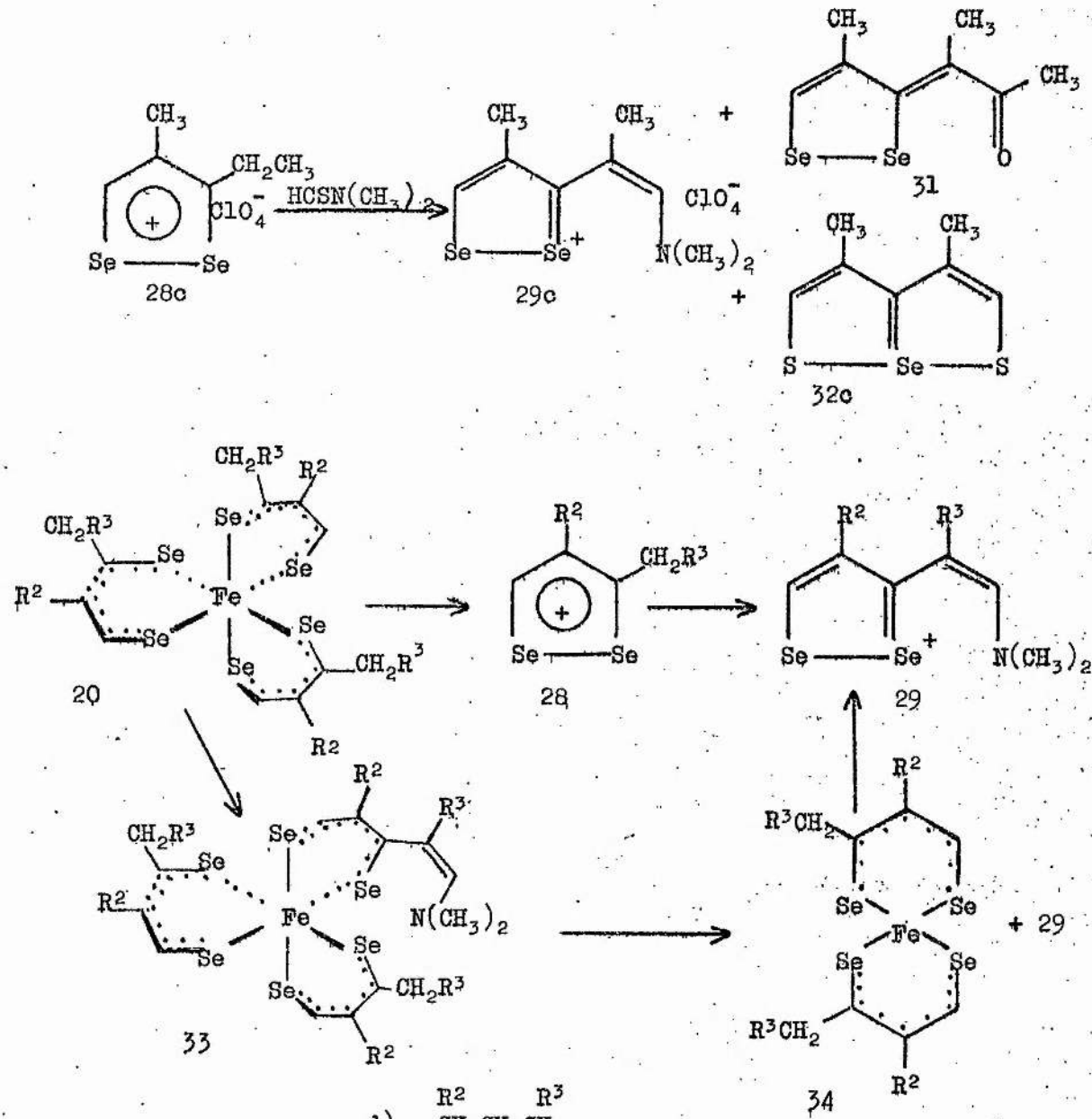
$O^{11,16}$] heptadeca-$\triangle^{3,8}$,$\triangle^{11,16}$-diene (21) was obtained.

The free 1,3-diselenoketones (22) are presumably formed initially in the reactions between the 1,3-diketones (17) and hydrogen selenide but either immediately dimerise to the 2,4,6,8-tetraselenaadamantanes (19), are oxidised to the 1,2-diselenolium cations (18) or are trapped by the metal ion to give the tris(1,3-diselenato) iron (III) complexes (20).

It is inexplicable that 2-hydroxymethylene cyclohexanone (17d) should give tris(2-selenoformylcyclohexane-1-selenato) iron (III) (20d) when, under identical conditions, the similarly substituted 2-hydroxymethylene-pentane-3-one (17c) gave bis(3-ethyl-4-methyl-1,2-diselenolium) tetrachloroferrate (II) (18c). Also, attempted preparations of bis(3-ethyl-4-methyl-1,2-dithiolium) tetrachloroferrate (II) (23) by reaction of 2-hydroxymethylene-pentane-3-one (17c) with hydrogen sulphide using the same procedure resulted in neither the formation of the required compound (23) nor in the formation of tris(1-thiolo-2-methyl-pent-1-ene-3-thione) iron (III) (24). According to Martin,[113] tris(4-thiolopent-3-ene-2-thione) iron (III) (25), bis(3,5-dimethyl-1,2-dithiolium) tetrachloroferrate (II) (26), and 1,3,5,7-tetramethyl-2,4,6,8-tetrathia-adamantane (27) can all separate consecutively or simultaneously when acetylacetone is reacted with hydrogen sulphide and iron (II) in ethanolic hydrogen bromide. It is therefore likely that the course of the reaction between a 1,3-diketone, iron (III) chloride, and hydrogen sulphide or hydrogen selenide in ethanolic hydrogen chloride will be particularly sensitive to the substitution pattern of the 1,3-diketone and to whether hydrogen sulphide or hydrogen selenide is used.

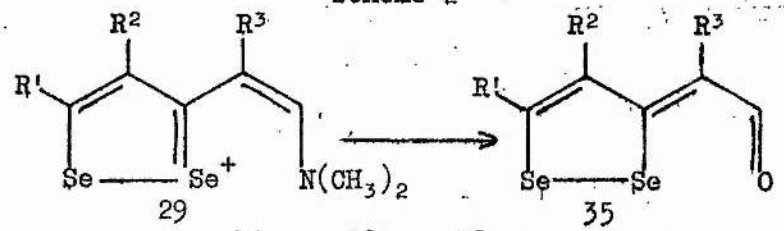
(3) 1,2-Diselenolium Perchlorates (28),

The tetrachloroferrate (II) anion in the salts (18) was readily exchanged for perchlorate anion to give the corresponding 1,2-diselenolium perchlorates (28).



d) $R^2 = -CH_2CH_2CH_2-$, R^3 = —
e) $R^2 = H$, $R^3 = H$

Scheme 2



	R'	R^2	R^3
a)	CH_3	H	H
b)	Ph	H	H
c)	H	CH_3	CH_3
d)	H	$-CH_2CH_2CH_2-$	
e)	H	H	H
f)	Ph	H	$COCH_3$

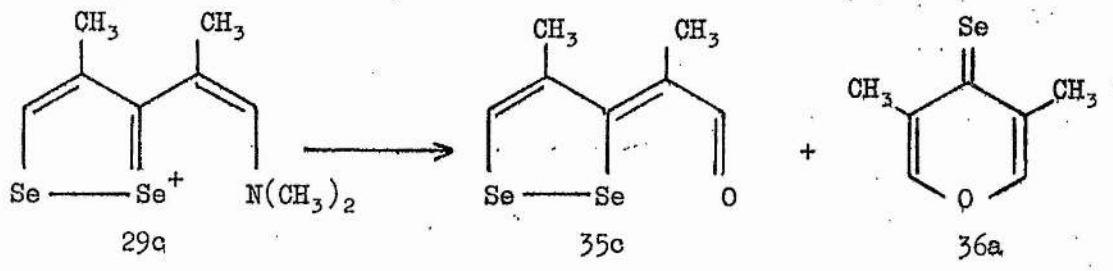
(4) 3-(2-Dimethylaminovinyl)-1,2-Diselenolium Salts (29).

Condensation of the 1,2-diselenolium perchlorates (28) with dimethylthioformamide resulted in formation of the corresponding salts (29). A crystalline salt, 3-(2-dimethylamino-1-methylvinyl)-4-methyl-1,2-diselenolium perchlorate (29c), could be obtained only from 3-ethyl-4-methyl-1,2-diselenolium perchlorate (28c), the perchlorates (28a) and (28b) affording dark red oils which could not be crystallised. These oils were used immediately in further reactions.

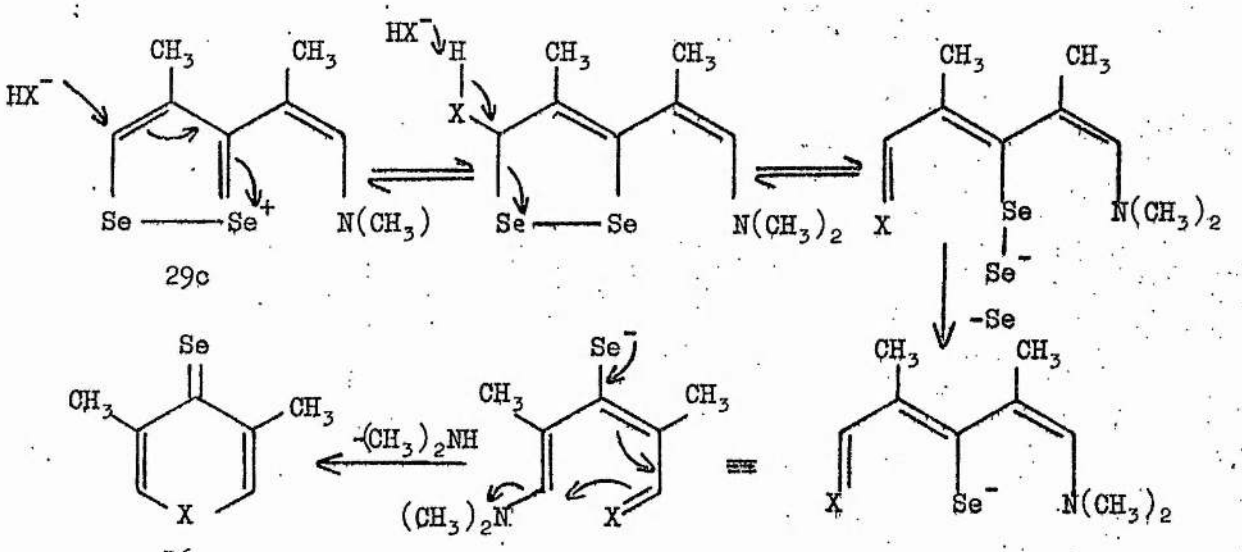
3-Methyl-5-phenyl-1,2-diselenolium perchlorate (28b) afforded a mixture of two salts (29b) and (29f) when condensed with dimethylthioformamide. The acetylated salt (29f) is presumably formed by an initial acetylation (scheme 1) of the perchlorate (28b) giving the intermediate (30) which then condenses with dimethylthioformamide.

Low yields of 3-(1-acetylethylidene)-4-methyl-3H-1,2-diselenole (31) and 3,4-dimethyl-1,6-dithia-6a-selenapentalene (32c) were isolated from the condensation of 3-ethyl-4-methyl-1,2-diselenolium perchlorate (28c) with dimethylthioformamide as well as the expected salt (29c). 3-(1-Acetylethylidene)-4-methyl-3H-1,2-diselenole (31) is simply the acetylation product of the perchlorate (28c). The mechanism of the formation of 3,4-dimethyl-1,6-dithia-6a-selenapentalene (32c) must involve reaction of either free sulphide ion liberated in the course of the condensation, or dimethylthioformamide acting as a sulphur donor, with the salt (29c). It will be shown later that selenium in the 1- or 6-position of a 6a-thiathiophthene ring can be readily exchanged for sulphur provided the adjacent carbon atom is unsubstituted.

Reaction of the tris(1,3-diselenato) iron (III) complexes (20) with phosphoryl chloride and dimethylthioformamide also resulted in condensation giving red oils containing the corresponding cations (29). The reaction, which must involve an oxidation, can proceed by either of two mechanisms (scheme 2). An initial oxidation of the tris(1,3-diselenato)



29a 35c 36a

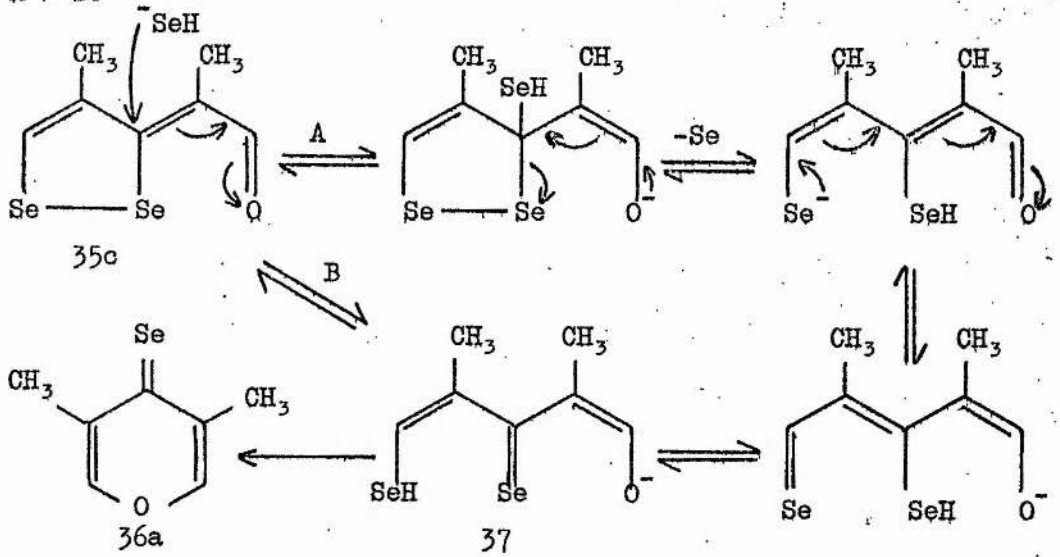


29c

36

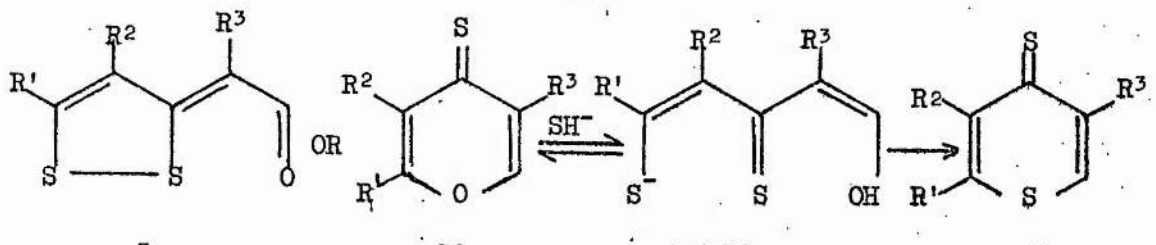
a) X = O
b) X = S
c) X = Se

Scheme 3



35c 36a 37

Scheme 4



5 38 39 40

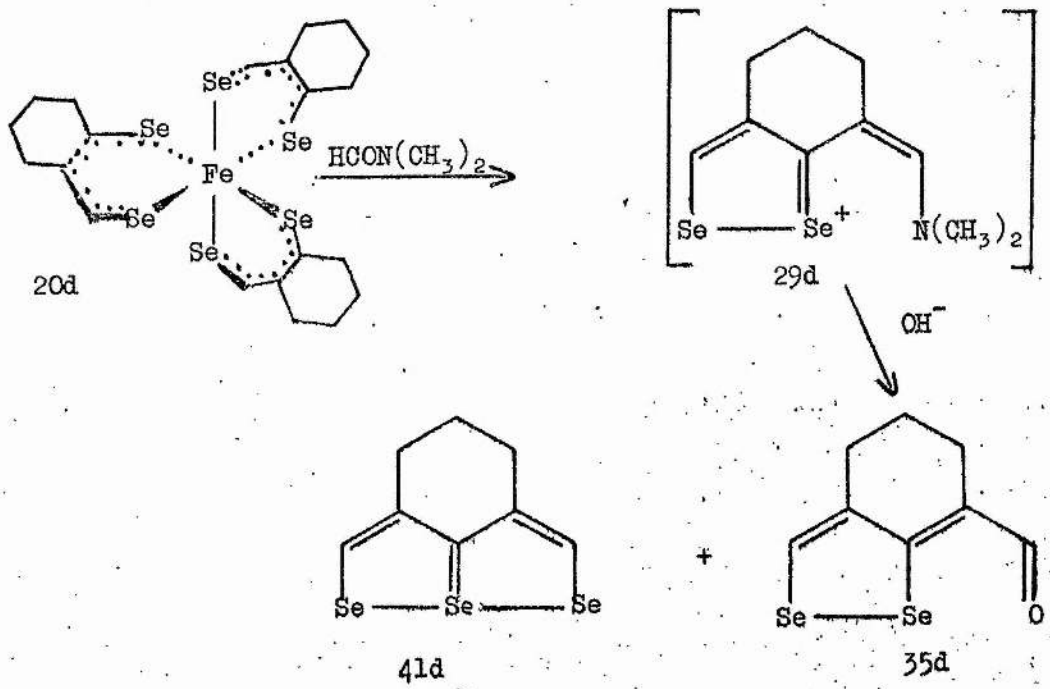
iron (III) complexes (20) would give the cations (28) which would then condense normally with the Vilsmeier reagents. Alternatively, an initial condensation giving products such as (33) could be envisaged followed by an oxidation to the cation (29) and the square planar complex (34). Reaction with the square planar complex (34) might then proceed in a stepwise condensation-oxidation manner until complete. The nature of the oxidising agent in this reaction is unknown and obviously much work is required in this area. To avoid the possibility of sulphur/selenium exchange, it was found better to condense tris(2-selenoformylcyclohexane-1-selenato) iron (III) (20d) with dimethylformamide rather than dimethylthioformamide. Tris(3-selenobut-1-ene-1-selenato) iron (III) (20e) would not, however, condense with dimethylformamide.

(5) 3-Acylmethylene-3H-1,2-Diselenoles (35).

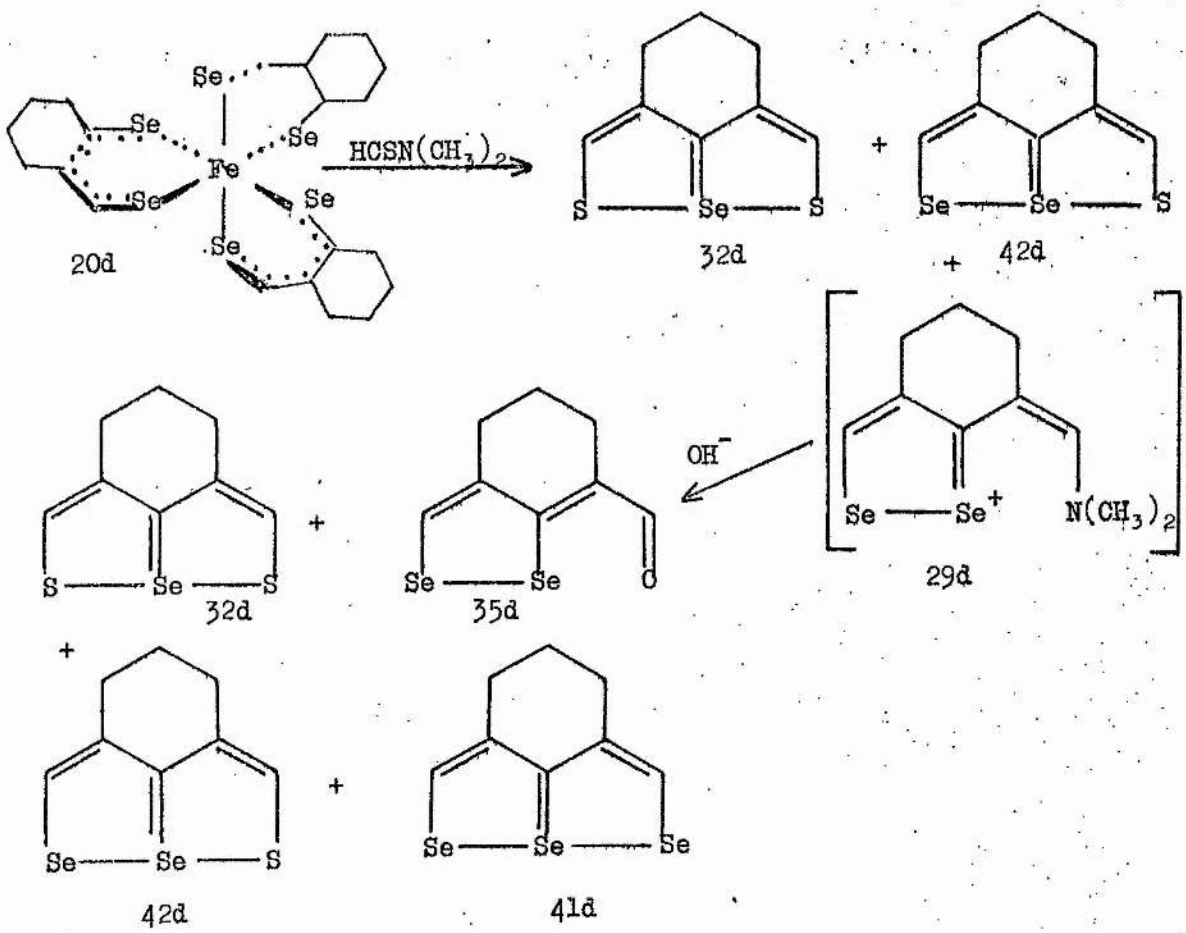
Solvolysis of the 3-(2-dimethylaminovinyl)-1,2-diselenolium salts (29) with aqueous sodium hydroxide gave the corresponding 3-acylmethylene-3H-1,2-diselenoles (35).

3-(1-Formyl-1-acetylmethylene)-5-phenyl-3H-1,2-diselenole (35f) was also isolated during the preparation of 3-formylmethylene-5-phenyl-3H-1,2-diselenole (35b) since condensation of 3-methyl-5-phenyl-1,2-diselenolium perchlorate (28b) with dimethylthioformamide afforded a mixture of the two salts (29b) and (29f).

The reaction between 3-(2-dimethylamino-1-methylvinyl)-4-methyl-1,2-diselenolium perchlorate (29c) and aqueous sodium hydroxide afforded 3,5-dimethyl-4H-pyran-4-selenoketone (36a) as well as the expected 3-acylmethylene-3H-1,2-diselenole (35c). 3-(1-Formylethylidene)-4-methyl-3H-1,2-diselenole (35c) did not react with aqueous hydroxide when subjected to identical conditions as was used for its preparation from the Vilsmeier salt (29c). There are therefore three possible mechanisms for the formation of 3,5-dimethyl-4H-pyran-4-selenoketone (36a) in this reaction. Nucleophilic attack by hydroxide anion (scheme 3, X=O) at the



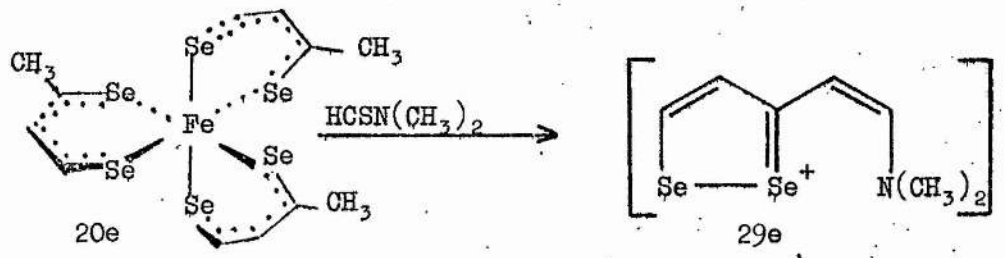
Scheme 5



Scheme 6

5-position of the 1,2-diselenolium ring of the salt (29c) leading to ring opening, rearrangement, and elimination of dimethylamine on ring closure is the most probable mechanism. The two other possibilities involve degradation of the salt (29c) resulting in formation of free hydroselenide anion which could then attack 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole (35c) (scheme 4). Nucleophilic attack (route A), or a reductive cleavage of the selenium-selenium bond (route B), would give the anion (37) which could eliminate hydroselenide anion on ring closure. However, 3-acylmethylene-3H-1,2-dithioles (5)[4,6,15] and 4H-pyran-4-thiones (38)[3-6] both form 4H-thiopyran-4-thiones (40) on reaction with sodium sulphide or hydrosulphide. Reaction in both cases must take place via anions of type (39) which eliminate hydroxide rather than hydrosulphide anion. A mechanism for the formation of 3,5-dimethyl-4H-pyran-4-selenoketone (36a) involving hydroselenide ion (scheme 4) must involve the intermediate anion (37) which, by analogy, would be expected to eliminate hydroxide ion and form 3,5-dimethyl-4H-selenopyran-4-selenoketone (36c). This is not observed and a mechanism involving nucleophilic attack at the 5-position of the 1,2-diselenolium ring (scheme 3) is therefore more probable.

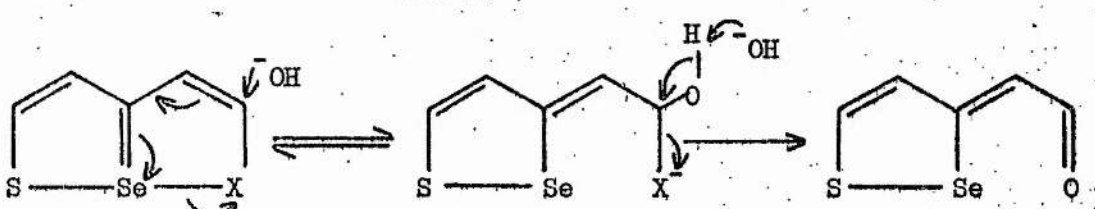
Solvolysis by hydroxide of the cation (29d) obtained by condensation of tris(2-selenoformylcyclohexane-1-selenato) iron (III) (20d) with dimethylformamide (scheme 5) afforded 4,5-dihydro-3H-benzo[c,d]1,6,6a-triselenapentalene (41d) as well as the expected 3-formyl-5,6-dihydro-4H-benzo[c][1,2] diselenole (35d). Degradation must take place, either during the condensation step or the solvolysis step, resulting in formation of free hydroselenide anion which then reacts with the cation (29d) to form the 1,6,6a-triselenapentalene (41d). Using dimethylthioformamide in the condensation step, complications arose because of the occurrence of sulphur/selenium exchange. Thus (scheme 6) a mixture of 4,5-dihydro-3H-benzo[c,d]1,6-dithia-6a-selenapentalene (32d) and 4,5-dihydro-3H-benzo[c,d]1-thia-6,6a-diselenapentalene (42d) in the ratio 9:1 was isolated at the condensation stage. Subsequent solvolysis by hydroxide of the



20e 29e

32e 42e 43 35e

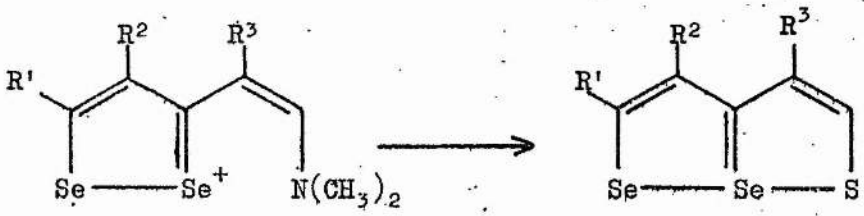
Scheme 7



42e X=Se
32e X=S

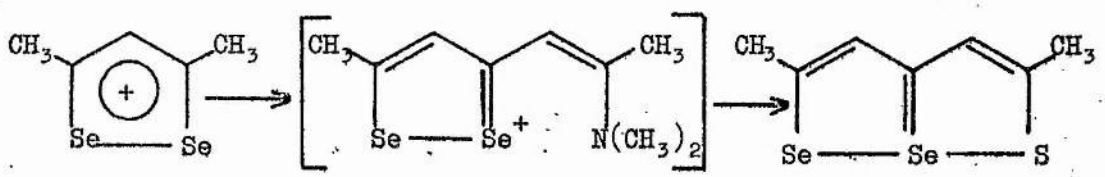
Scheme 8

43



29 42

	R'	R^2	R^3
a)	CH_3	H	H
b)	Ph	H	H
c)	H	CH_3	CH_3
d)	H	$-CH_2CH_2CH_2-$	
e)	H	H	H
f)	Ph	H	$COCH_3$



28a 29g 42g

+ $C_{12}H_{12}S_2Se$

44

resulting oil containing the cation (29d) afforded a mixture of the three analogues (32d), (41d), and (42d) in the ratio 1:1:4 as well as 3-formyl-5,6-dihydro-4H-benzo[c][1,2]diselenole (35d).

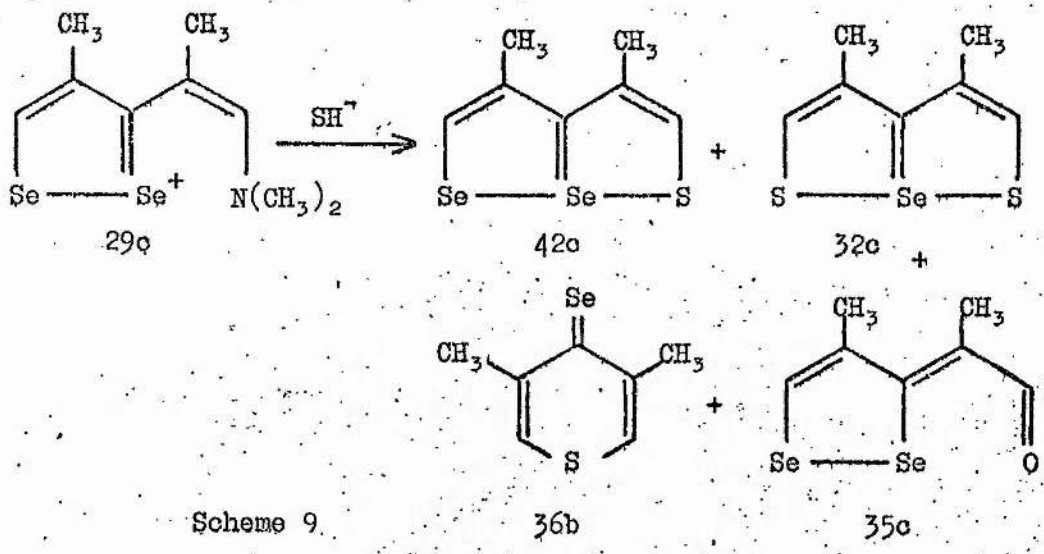
The problem of degradation followed by sulphur/selenium exchange was also evident in the preparation of 3-formylmethylene-3H-1,2-diselenole (35e) (scheme 7). A mixture of 1-thia-6,6a-diselenapentalene (42e) and 1,6-dithia-6a-selenapentalene (32e) in the ratio 2:1 was obtained. The N.M.R. spectrum showed the presence (ca. 10%) of an impurity in the 3-formylmethylene-3H-1,2-diselenole (35e) by doublets at δ 8.39 and δ 7.68. The presence of a peak at m/e 192 in the mass spectrum and the position of the peaks in the N.M.R. spectrum suggest this impurity to be 3-formylmethylene-3H-1,2-thiaselenole (43). Nucleophilic attack by hydroxide ion on either 1,6-dithia-6a-selenapentalene (32e) or 1-thia-6,6a-diselenapentalene (42e) (scheme 8) would result in formation of 3-formylmethylene-3H-1,2-thiaselenole (43).

(6) 1-Thia-6,6a-Diselenapentalenes (42).

The 1-thia-6,6a-diselenapentalenes (42) were obtained by treatment of solutions containing the corresponding 3-(2-dimethylaminovinyl)-1,2-diselenolium cations (29) with aqueous sodium hydrogen sulphide.

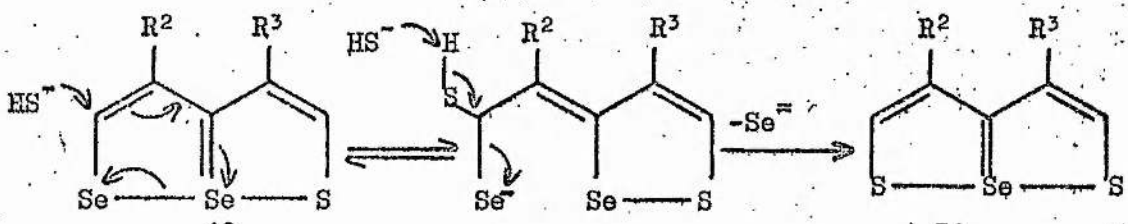
3,5-Dimethyl-1,2-diselenolium perchlorate (28a) was also condensed with dimethylthioacetamide giving a dark red oil containing the cation (29g). Solvolysis of this oil with aqueous sodium hydrogen sulphide afforded the expected 2,5-dimethyl-1-thia-6,6a-diselenapentalene (42g) and also a compound (44) of molecular formula $C_{12}H_{12}SeS_2$ whose structure could not be deduced.

The reaction of sodium hydrogen sulphide with 3-(2-dimethylamino-1-methylvinyl)-4-methyl-1,2-diselenolium perchlorate (29c) (scheme 9) produced a 1:1 mixture of 3,4-dimethyl-1-thia-6,6a-diselenapentalene (42c) and 3,4-dimethyl-1,6-dithia-6a-selenapentalene (32c) which could not be separated by



29c 42c 32c 36b 35c

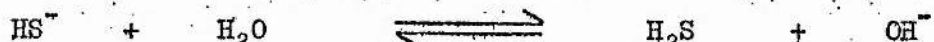
Scheme 9



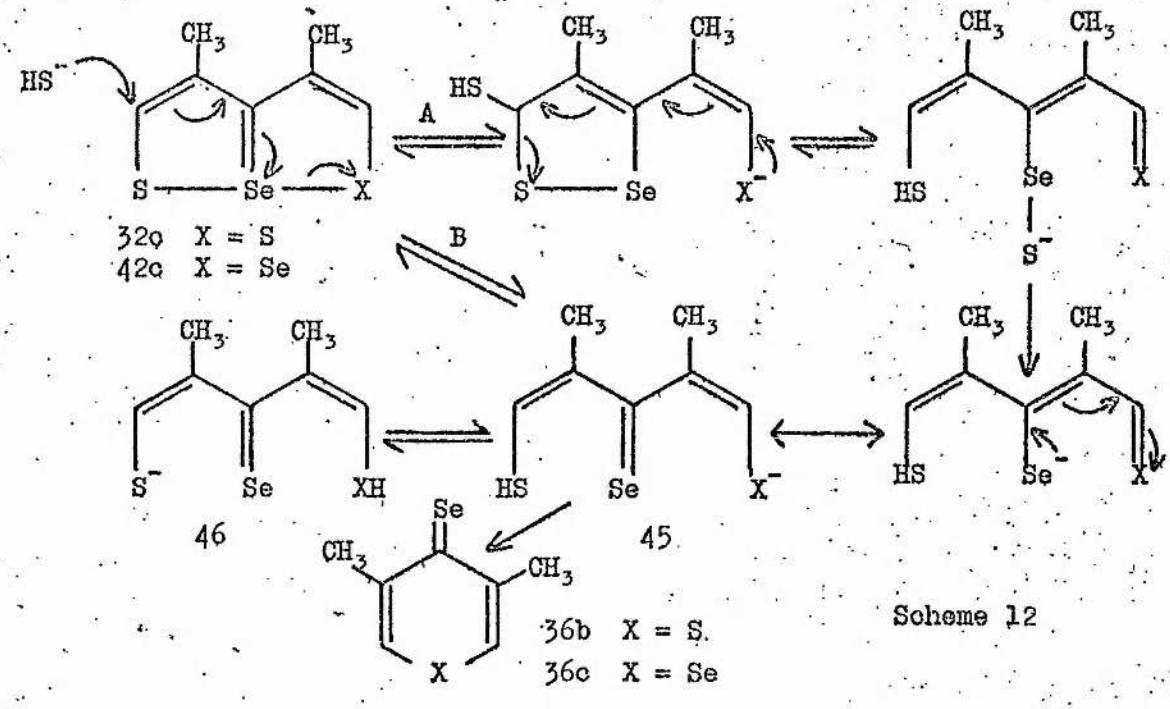
42 32

c) $R^2 = CH_3$, $R^3 = CH_3$
d) $R^2, R^3 = -CH_2CH_2CH_2-$
e) $R^2 = H$, $R^3 = H$

Scheme 10



Scheme 11



32c X = S
42c X = Se

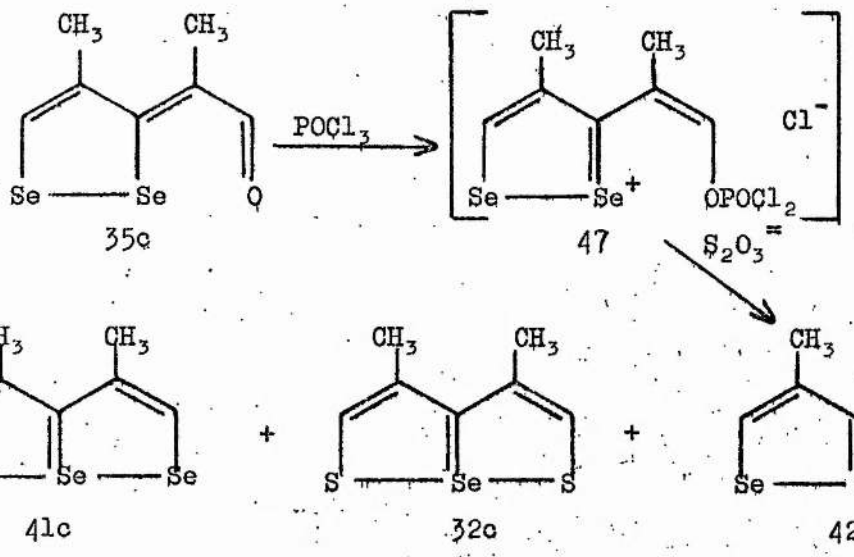
46 45

36b X = S
36c X = Se

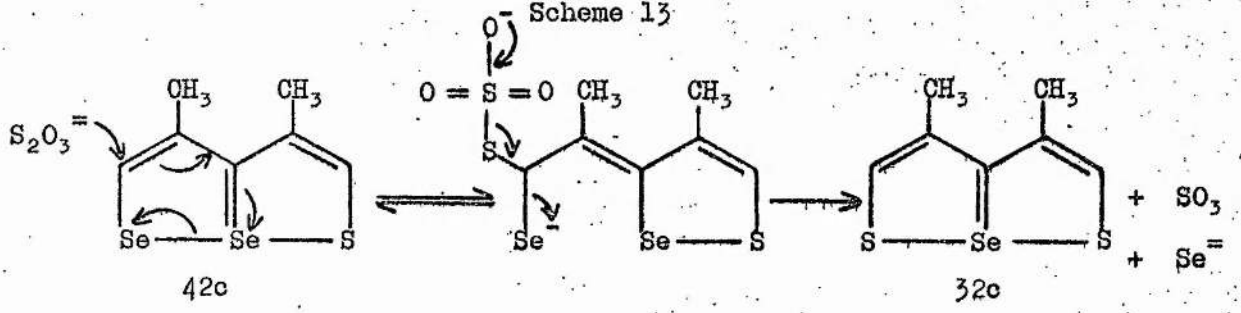
Scheme 12

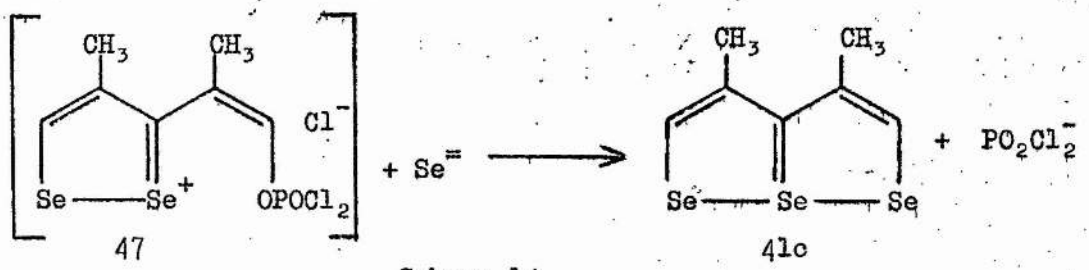
chromatography or crystallisation. Nucleophilic attack by hydrosulphide ion on the initially formed 3,4-dimethyl-1-thia-6,6a-diselenapentalene (42c) (scheme 10) followed by preferential elimination of selenide anion explains the formation of 3,4-dimethyl-1,6-dithia-6a-selenapentalene (32c). A small amount (3.6%) of 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole (35c) also isolated from the reaction mixture presumably results from solvolysis of the salt (29c) with hydroxide ion which would be in equilibrium with hydrosulphide ion (scheme 11). Several mechanisms can be proposed for the formation of 3,5-dimethyl-4H-thiopyran-4-selenoketone (36b) in this reaction (scheme 9). Nucleophilic attack of hydrosulphide anion at the 5-position of the 1,2-diselenolium ring of the salt (29c) (scheme 3, X = S) is the favoured mechanism, analogous to attack by hydroxide leading to 3,5-dimethyl-4H-pyran-4-selenoketone (36a) (scheme 3, X = O). Alternatively, 3,5-dimethyl-4H-thiopyran-4-selenoketone (36b) could be formed (scheme 12) by nucleophilic attack (route A) or by a reductive mechanism (route B) on either 3,4-dimethyl-1,6-dithia-6a-selenapentalene (32c) or 3,4-dimethyl-1-thia-6,6a-diselenapentalene (42c). Either mechanism involves the anion (45) or its tautomer (46) as an intermediate which, if derived from 3,4-dimethyl-1-thia-6,6a-diselenapentalene (42c) (X = Se), would be expected to eliminate hydrosulphide ion and form 3,5-dimethyl-4H-selenopyran-4-selenoketone (36c) since selenide is a better nucleophile than sulphide. No 3,5-dimethyl-4H-selenopyran-4-selenoketone (36c) was observed and it is therefore concluded that the mechanism of the formation of 3,5-dimethyl-4H-thiopyran-4-selenoketone (36b) involves a nucleophilic attack by hydrosulphide ion on 3-(2-dimethylamino-1-methylvinyl)-4-methyl-1,2-diselenolium perchlorate (29c) (scheme 3, X = S).

In a further attempt to synthesise 3,4-dimethyl-1-thia-6,6a-diselenapentalene (42c), 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole (35c) was treated with phosphoryl chloride in dimethyl-

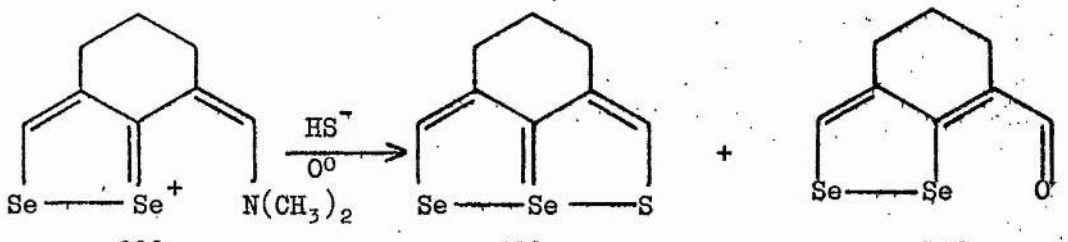


Scheme 13

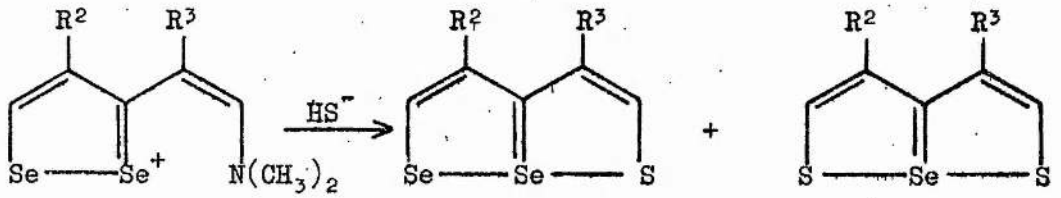




Scheme 14



Scheme 15



	R²	R³
d)	-CH₂CH₂CH₂-	
e)	H	H

Scheme 16

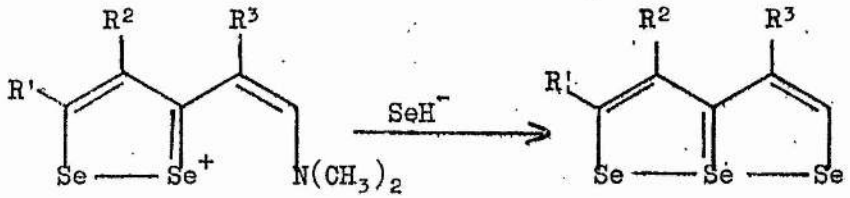
formamide and the resulting solution with aqueous sodium thiosulphate. This reaction surprisingly afforded (scheme 13) a mixture of the three analogues (32c), (41c), and (42c). 3,4-Dimethyl-1,6-dithia-6a-selenapentalene (32c) is presumed to arise by nucleophilic attack of thiosulphate ion (scheme 14) on the initially formed 3,4-dimethyl-1-thia-6,6a-diselenapentalene (42c). The liberated selenide ion in turn attacks the intermediate (47) producing 3,4-dimethyl-1,6,6a-triselenapentalene (41c). The ease of replacing selenium in the 1- or 6-position by sulphur emphasises the susceptibility of the 2- and 5- carbon atoms to nucleophilic attack provided these carbon atoms are unsubstituted.

4,5-Dihydro-3H-benzo[c,d]1-thia-6,6a-diselenapentalene (42d) and 3-formyl-5,6-dihydro-4H-benzo[c][1,2]-diselenole (35d) were obtained (scheme 15) by solvolysis of the cation (29d) with aqueous sodium hydrogen sulphide at $0^{\circ}C$. 3-Formyl-5,6-dihydro-4H-benzo[c][1,2]-diselenole (35d) presumably results from solvolysis of the salt (29d) with hydroxide ion which would be in equilibrium with hydrosulphide ion (scheme 11). Solvolysis of the cations (29d) and (29e) by hydrosulphide ion at room temperature afforded (scheme 16) mixtures of the corresponding analogues (32) and (42). The 1,6-dithia-6a-selenapentalenes (32) are considered to arise by nucleophilic attack of hydrosulphide ion at the 5-position of the 1-thia-6,6a-diselenapentalenes (42) (scheme 10).

(7) 1,6,6a-Triselenapentalenes (41).

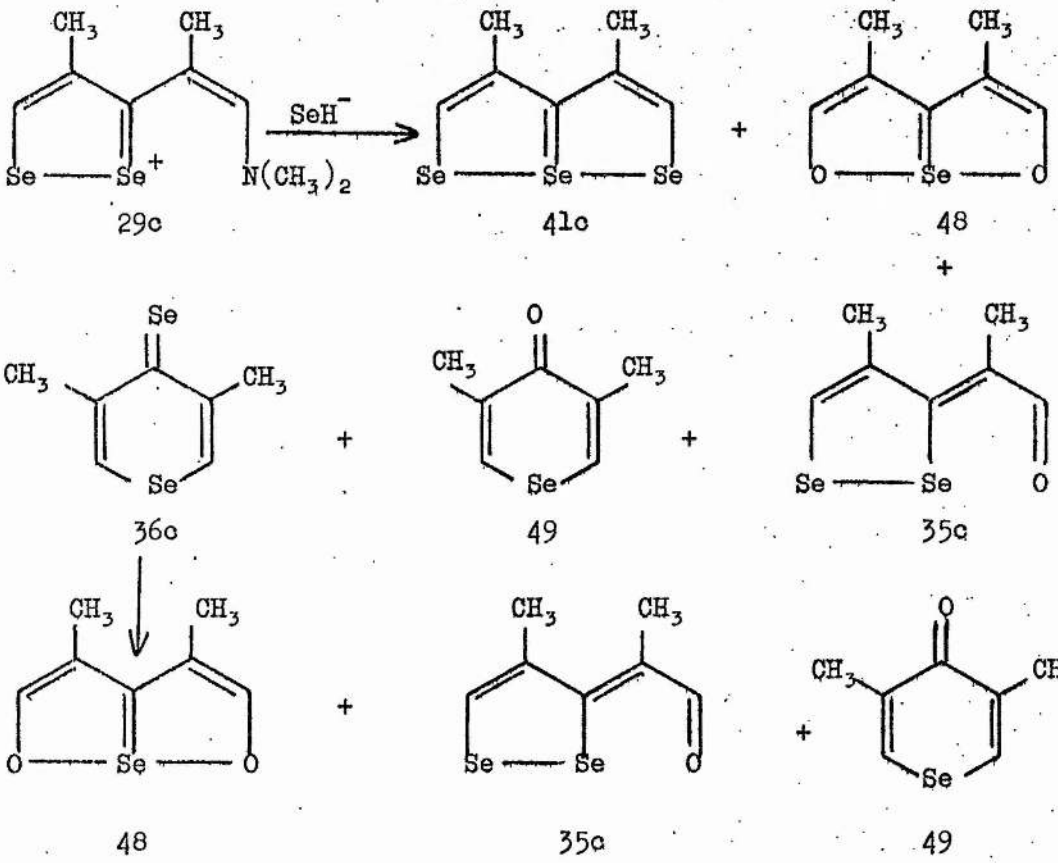
Treatment of solutions containing the 3-(2-dimethylaminovinyl)-1,2-diselenolium cations (29) with aqueous sodium hydrogen selenide afforded the corresponding 1,6,6a-triselenapentalenes (41).

The reaction between 3-(2-dimethylamino-1-methylvinyl)-4-methyl-1,2-diselenolium perchlorate (29c) and aqueous sodium hydrogen selenide was complicated owing to the nature of the products. A mass spectrum of an aliquot of the benzene extracts showed the major product to be



29 41

	R'	R²	R³
a)	CH_3	H	H
b)	Ph	H	H
c)	H	CH_3	CH_3
d)	H	$-CH_2CH_2CH_2-$	
e)	H	H	H
f)	Ph	H	$COCH_3$

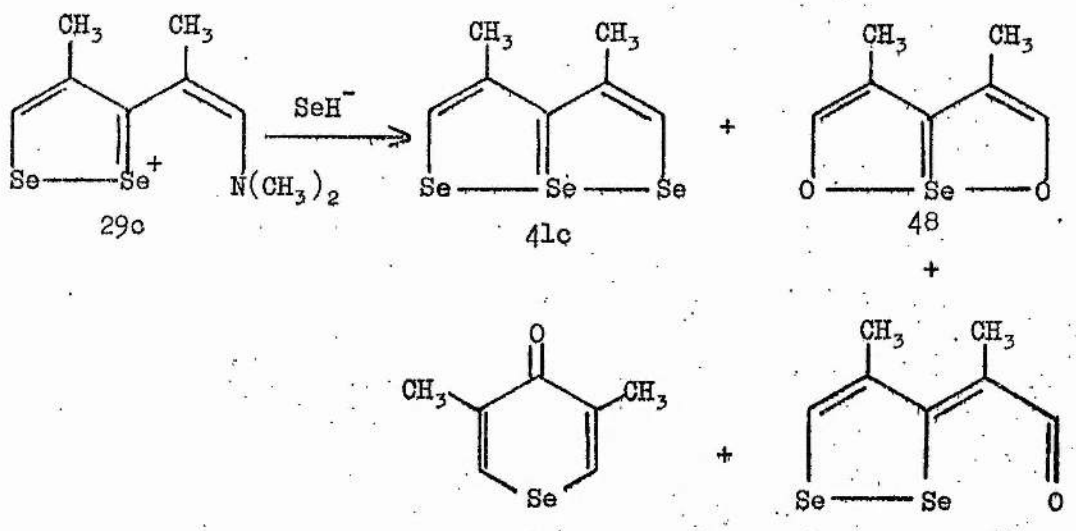


Scheme 17

3,5-dimethyl-4H-selenopyran-4-selenoketone (36c). The benzene extracts, however, afforded (scheme 17) five products: 3,4-dimethyl-1,6,6a-triselenapentalene (41c) (3%), 3,4-dimethyl-1,6-dioxa-6a-selenapentalene (48) (3.9%), 3,5-dimethyl-4H-selenopyran-4-selenoketone (36c) (47%), 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole (35c) (9.4%), and 3,5-dimethyl-4H-selenopyran-4-one (49) (7.3%). 3,5-Dimethyl-4H-selenopyran-4-selenoketone (36c) was found to be unstable as a crystalline solid and gave (scheme 17) 3,4-dimethyl-1,6-dioxa-6a-selenapentalene (48) (1.0%), 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole (35c) (12%) and 3,5-dimethyl-4H-selenopyran-4-one (49) (23%) when left as a solid overnight.

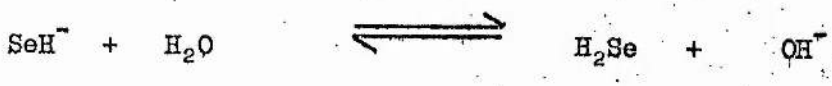
Extraction of the reaction mixture with chloroform showed 3,5-dimethyl-4H-selenopyran-4-selenoketone to be unstable in this solvent, particularly when exposed to strong sunlight. The chloroform extracts afforded (scheme 18) 3,4-dimethyl-1,6,6a-triselenapentalene (41c) (1.1%), 3,4-dimethyl-1,6-dioxa-6a-selenapentalene (48) (1.1%), 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole (35c) (10%), and 3,5-dimethyl-4H-selenopyran-4-one (49) (77%).

3-(2-Dimethylamino-1-methylvinyl)-4-methyl-1,2-diselenolium perchlorate (29c) reacts with aqueous sodium hydrogen selenide to form initially the expected 3,4-dimethyl-1,6,6a-triselenapentalene (41c) (ca. 2%), 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole (35c) (ca. 10%), presumably arising by solvolysis of the Vilsmeier salt (29c) with hydroxide ion which would be present because of the equilibrium (scheme 19) with hydroselenide ion, and 3,5-dimethyl-4H-selenopyran-4-selenoketone (36c). The selenoketone (36c) could be formed by nucleophilic attack of hydroselenide ion at the 5-position of the salt (29c) (scheme 3, X=Se), or alternatively from the initially formed 3,4-dimethyl-1,6,6a-triselenapentalene (41c) (scheme 20) either by nucleophilic attack of excess hydroselenide ion (route A) or a reductive

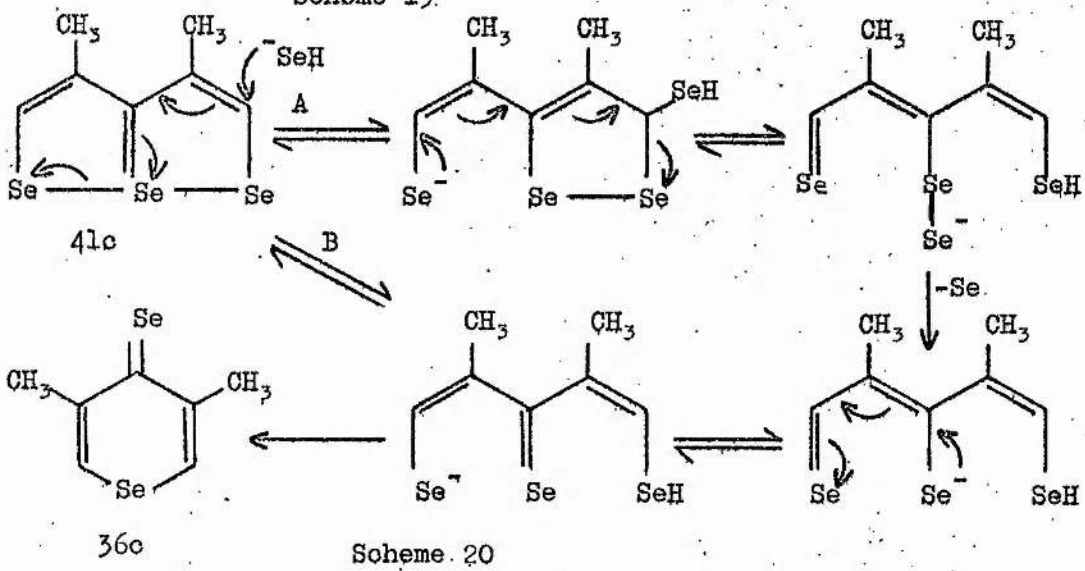


29c 41c 48 49 35a

Scheme 18

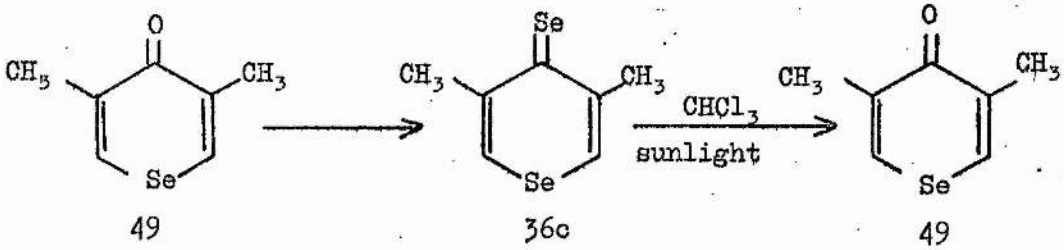


Scheme 19



41c 36c

Scheme 20



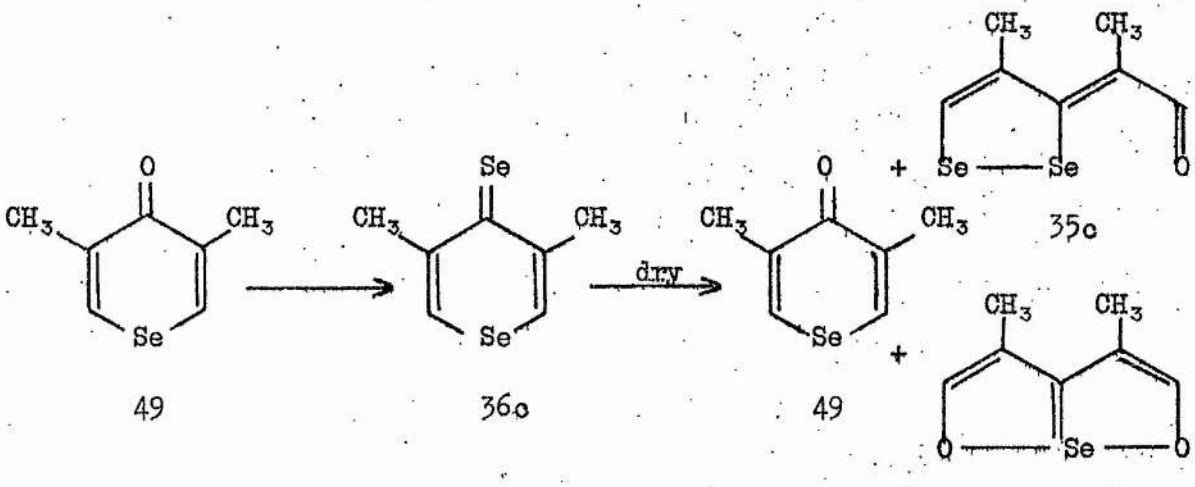
49 36c 49

Scheme 21

cleavage of the selenium-selenium bond (route B).

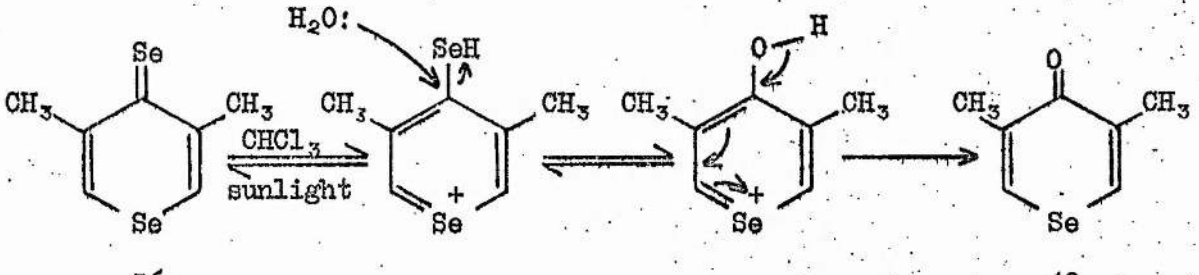
3,5-Dimethyl-4H-selenopyran-4-selenoketone (36c) was also obtained in 49% yield from the corresponding ketone (49). When extracted into chloroform and the solution exposed to sunlight (scheme 21), 3,5-dimethyl-4H-selenopyran-4-one (49) was recovered in 38% yield. If, however, the selenoketone (36c) was extracted into benzene, the benzene extracts evaporated to dryness and left for eighteen hours before chromatography, then the products (scheme 22) were substantially different. 3,4-Dimethyl-1,6-dioxa-6a-selenapentalene (48) (0.6%), 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole (35c) (13%), and 3,5-dimethyl-4H-selenopyran-4-one (49) (22%) were obtained, demonstrating that these three compounds must be derived from the selenoketone (36c).

3,5-Dimethyl-4H-selenopyran-4-selenoketone (36c), in chloroform solution saturated with water, was converted (scheme 21) exclusively to the corresponding ketone (49). This reaction was accelerated by strong sunlight and is therefore probably an acid catalysed hydrolysis (scheme 23). In benzene solution, the selenoketone (36c) was relatively stable, bubbling air through the solution for five hours resulted in no oxidation. The crystalline solid, however, afforded three compounds (scheme 22) presumably by atmospheric oxidation. 3,5-Dimethyl-4H-selenopyran-4-one (49) would result from attack by molecular oxygen at the 4-position of the selenoketone (36c). Radical attack by atmospheric oxygen at the 2-position of the ring (scheme 24) could also be envisaged leading to the diradical (50) which might then decompose in two ways. Loss of oxygen and rearrangement to the intermediate (51) which immediately tautomerises would afford 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole (35c). Intramolecular displacement of selenium by the oxygen atom of the diradical (50) would give the Arndt structure (52). Cleavage of the peroxide bond and rearrangement then leads to formation of 3,4-dimethyl-1,6-dioxa-6a-selenapentalene (48). Since a benzene solution



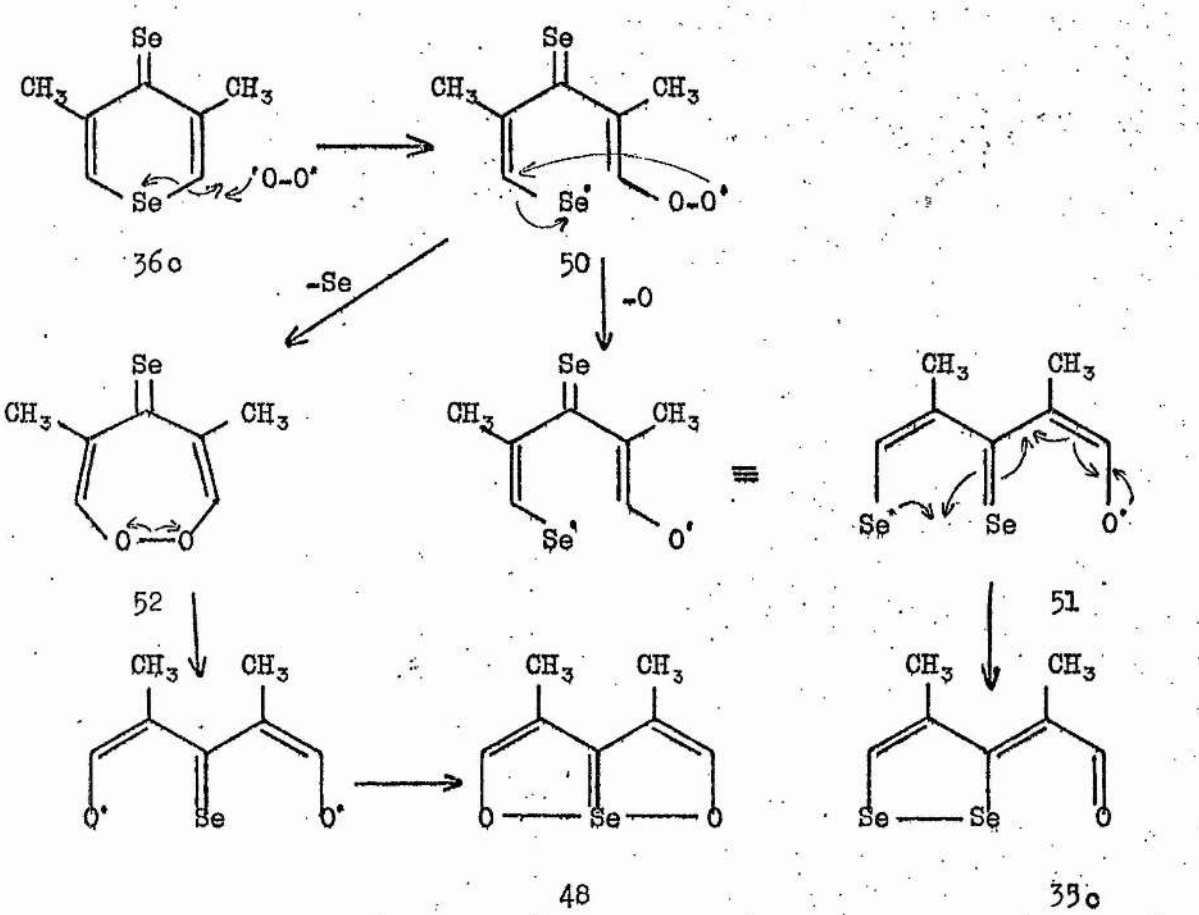
49 36c 49 35c 48

Scheme 22



36c 49

Scheme 23



36c 50 52 51 48 35c

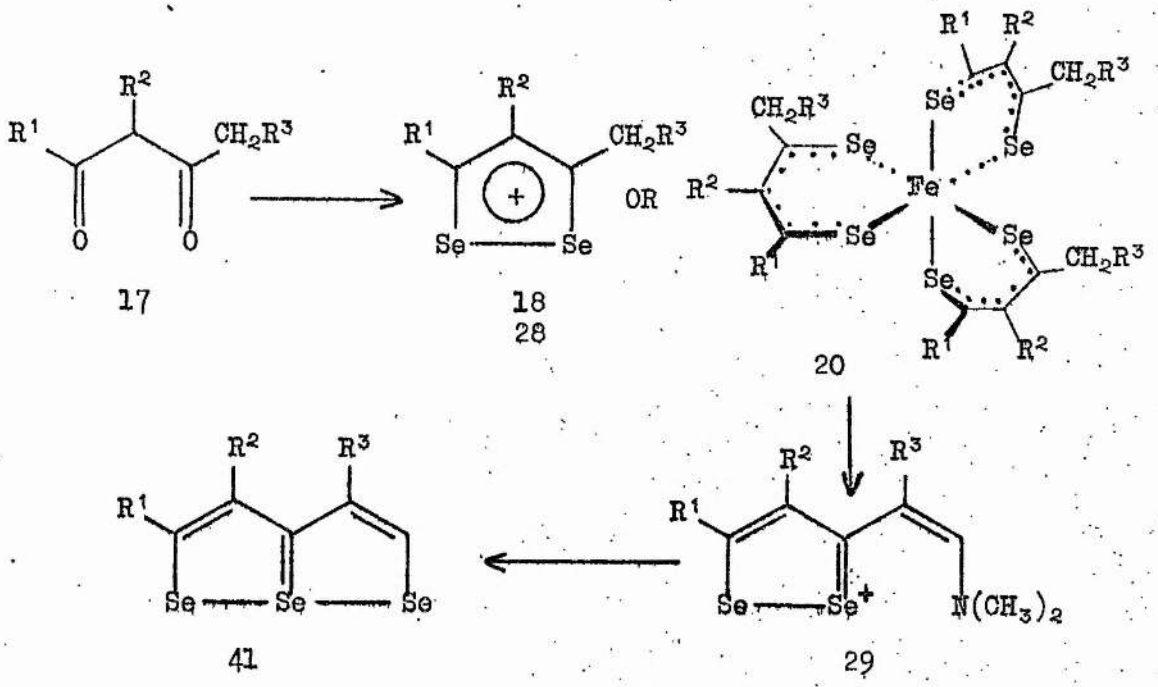
Scheme 24

of 3,5-dimethyl-4H-selenopyran-4-selenoketone (36c) was stable to atmospheric oxidation, it is likely that the radical reactions outlined in scheme 24 are surface reactions.

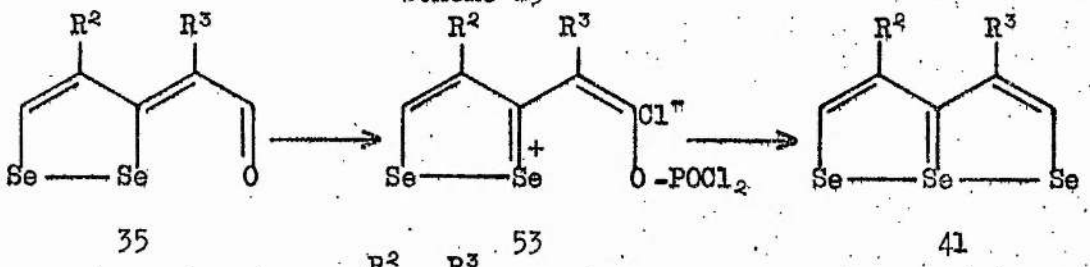
The parent 1,6,6a-triselenapentalene (41e) was obtained surprisingly without the complication of sulphur/selenium exchange although in very low yield.

The sequence (scheme 25): 1,3-diketone (17) ⟶ 1,2-diselenolium salt (18,28) or tris(1,3-diselenato) iron (III) complex (20) ⟶ 3-(2-dimethylaminovinyl)-1,2-diselenolium salt (29) and subsequent reaction with aqueous sodium hydrogen selenide thus provides a synthesis of 1,6,6a-triselenapentalenes (41), a novel class of heterocyclic compounds.

The 1,6,6a-triselenapentalenes (41c) and (41d) were also obtained (scheme 26) by treatment of the corresponding 3-acylmethylene-3H-1,2-diselenoles (35) in dimethylformamide at room temperature with phosphoryl chloride, and of the resulting solutions with aqueous potassium selenosulphate. Presumably the salts (53) are the reaction intermediates, in view of the mildness of the reaction conditions. In this context the selenosulphate ion may be regarded as a selenide ion co-ordinated to sulphur trioxide, a good leaving group in the presence of water. The required nucleophilic character of the selenide ion is retained in the selenosulphate ion to a sufficient degree but the reducing properties are absent. When potassium selenotrithionate was used in place of potassium selenosulphate, a lower yield of 3,4-dimethyl-1,6,6a-triselenapentalene (41c) was obtained. Thus, the selenotrithionate ion also retains the nucleophilic character of the selenide ion although to a lesser degree than the selenosulphate ion. When oxalyl chloride was used in place of phosphoryl chloride, 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole (35c) in chloroform gave an oil presumably containing the salt (54). Subsequent reaction with aqueous potassium selenosulphate afforded only a low yield of the corresponding 1,6,6a-triselenapentalene (41d).

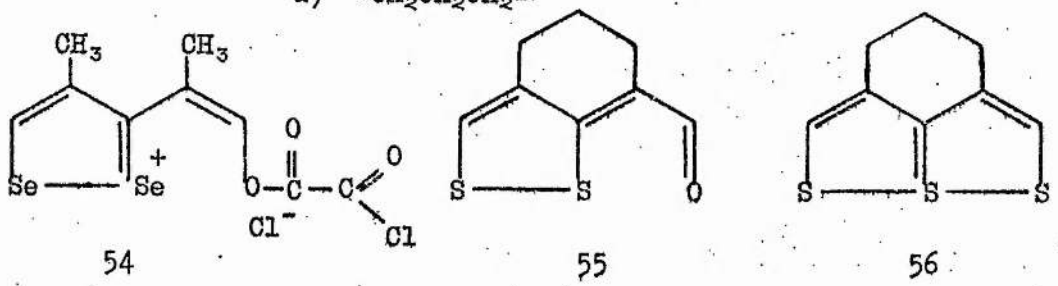


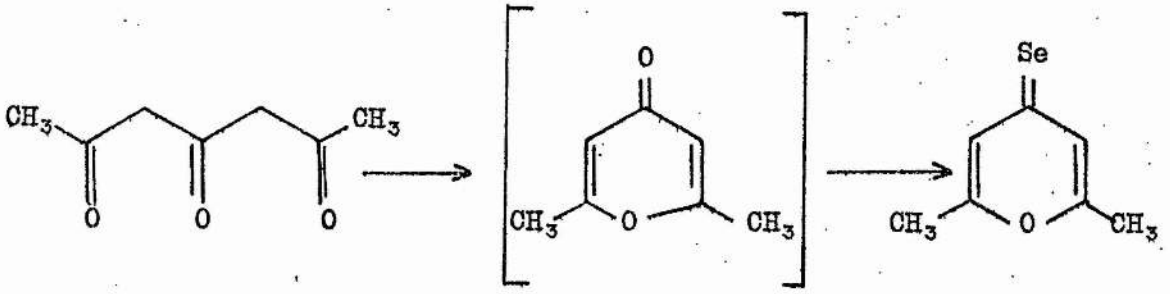
Scheme 25



c) CH_3 CH_3
d) $-CH_2CH_2CH_2-$

Scheme 26





An attempted preparation of 4,5-dihydro-3H-benzo[c,d]1,6,6a-triselenapentalene (41d) by reaction of aqueous sodium hydrogen selenide with 3-formyl-5,6-dihydro-4H-benzo[c][1,2]-diselenole (35d) resulted in recovery of the 1,2-diselenole (35d). Under similar conditions, 3-formyl-5,6-dihydro-4H-benzo[c][1,2]-dithiole (55) afforded an 80% yield of the corresponding 6a-thiathiophthene (56). This result is surprising since the reaction must proceed by a nucleophilic mechanism and hydroselenide ion is expected to be a better nucleophile than hydrosulphide ion.

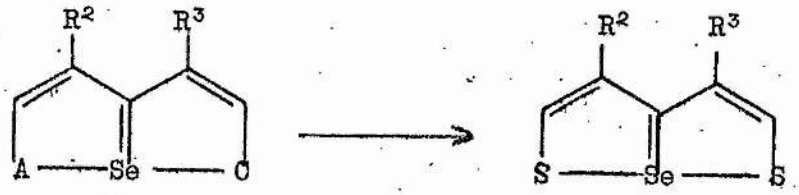
Parallel to Arndt's original synthesis[1] of 2,5-dimethyl-6a-thiathiophthene, a solution of heptane-2,4,6-trione in chlorobenzene was boiled with phosphorus pentaselenide. 2,6-Dimethyl-4H-pyran-4-selenoketone (58) was the only product formed, probably resulting from initial cyclisation to the ketone (57) and subsequent selenation by phosphorus pentaselenide.

(8) 1,6-Dithia-6a-Selenapentalenes (32).

The 1,6-dithia-6a-selenapentalenes (32c-e) were obtained by treatment of solutions containing mixtures of the corresponding analogues (59) with phosphorus pentasulphide. It is difficult to envisage how Pietra[55] could isolate the selenium analogue (60) from the reaction between 3-(1-acetylmethylene)- 5 -methyl-3H-1,2-diselenole (61) and phosphorus pentasulphide. In the reactions studied, selenium in the 2-position of a 3-acylmethylene-3H-1,2-diselenole (35) and in the 6a-position of a 6a-selenapentalene ring (59) has not been replaced with sulphur by the action of either phosphorus pentasulphide or aqueous sodium hydrogen sulphide. Selenium in the lateral 1- and 6-positions, however, is readily replaced by sulphur provided the adjacent carbon atom is unsubstituted.

(9) 3,4-Dimethyl-6a-Thia-1,6-Diselenapentalene (62).

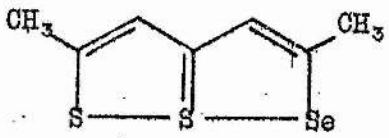
The possibility of synthesising 3,4-dimethyl-6a-thia-1,6-diselenapentalene (62) by a route parallel to that used for the preparation[99] of 1,6-dithia-6a-selenapentalenes (7) appeared attractive. 3,5-Dimethyl-4H-selenopyran-4-one (49) was thus converted readily into the corresponding



59 32

A,C = O,S or Se

	R^2	R^3
c)	CH_3	CH_3
d)	$-CH_2CH_2CH_2-$	
e)	H	H



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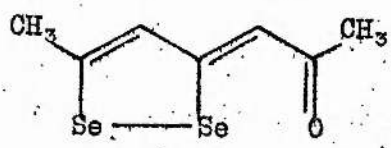

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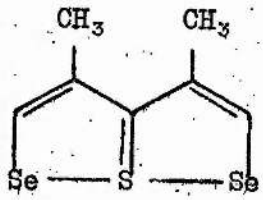

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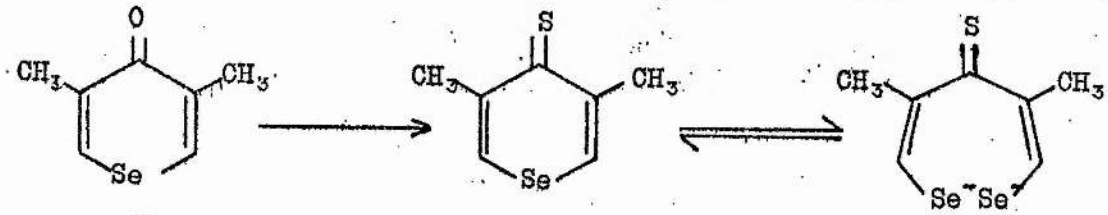
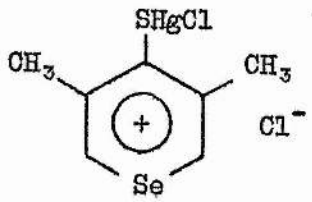
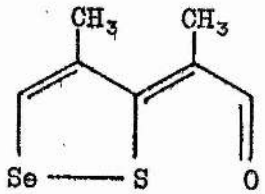


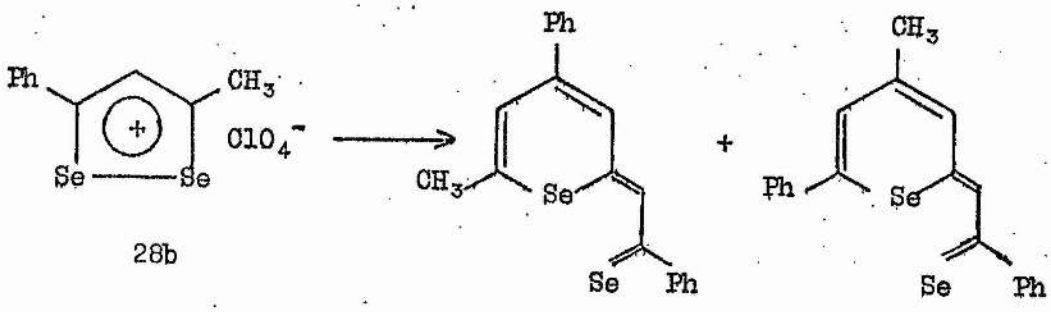
49 63 64



65



66

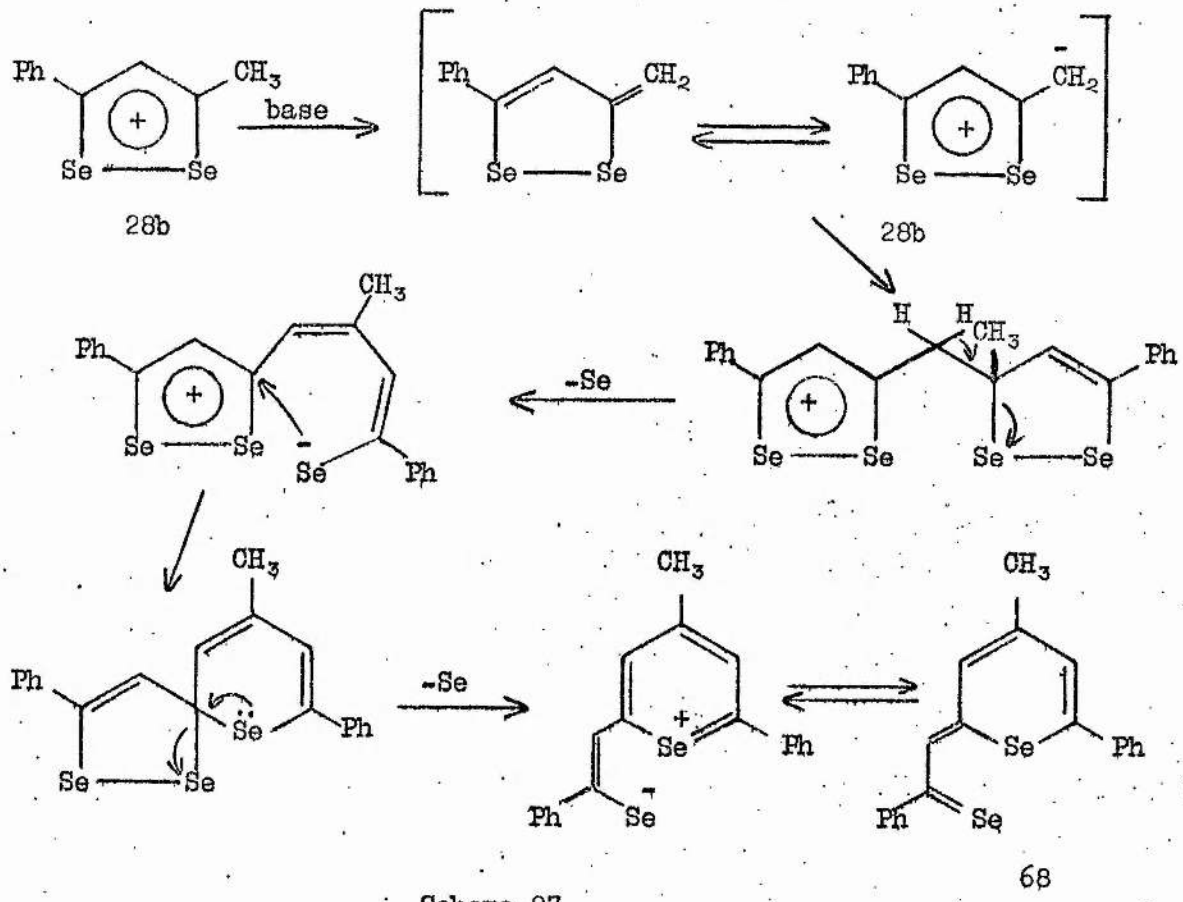


28b 67 68

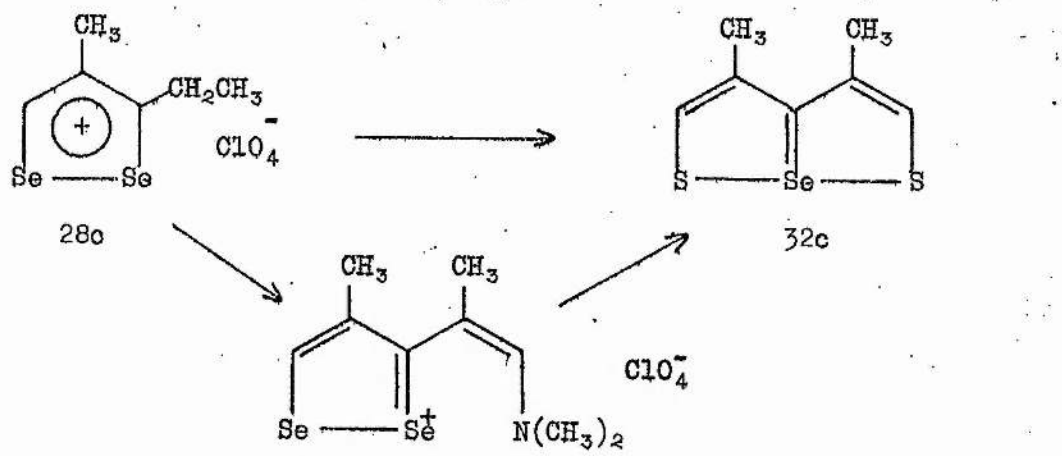
thione (63). Addition of aqueous sodium selenide to a solution of the thione (63) in dimethylsulphoxide gave a deep purple solution presumably containing the dianion (64) or related species. Attempted intramolecular oxidative coupling of the dianion (64) by aqueous potassium ferricyanide, however, resulted only in recovery of 3,5-dimethyl-4H-selenopyran-4-thione (63). A further route to 3,4-dimethyl-6a-thia-1,6-diselenapentalene (62), via 5-(1-formylethylidene)-4-methyl-5H-1,2-thiaselenole (66), was also investigated. The reaction of aqueous carbonate with the salt (65) resulted again in recovery of the thione (63). A 6a-thia-1,6-diselenapentalene remains the only analogue of the 6a-thiathiophthene system containing a combination of sulphur and selenium atoms that has not been synthesised.

(10) Condensation and Exchange Reactions.

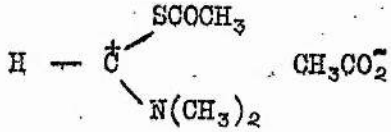
The reaction of 3-methyl-5-phenyl-1,2-diselenolium perchlorate (28b) with dimethylthioformamide in acetic anhydride at room temperature followed a different course from the expected condensation leading to 3-(2-dimethylaminovinyl)-5-phenyl-1,2-diselenolium perchlorate (29b). Self-condensation of the 1,2-diselenolium salt (28b) took place affording 4-phenyl-6-methyl-2-selenaphenacylidene-2H-selenopyran (67) and/or the 6-phenyl-4-methyl isomer (68) together with analogous compounds in which one selenium atom is replaced by a sulphur atom. With triethylamine in acetonitrile, self-condensation proceeded more rapidly by a mechanism (scheme 27) probably identical to that proposed by Leaver[158] for the self-condensation of 3-methyl-5-phenyl-1,2-dithiolium salts, giving the isomers (67) and (68) without the complication of sulphur/selenium exchange. 3,5-Dimethyl-1,2-diselenolium perchlorate (28a) did not self-condense using these conditions. After boiling 3-methyl-5-phenyl-1,2-diselenolium perchlorate (28b) in acetic anhydride with dimethylthioformamide, the conditions used for the preparation of the 3-(2-dimethylaminovinyl)-1,2-diselenolium perchlorates (29), no trace of the self-condensation product



Scheme 27



Scheme 28

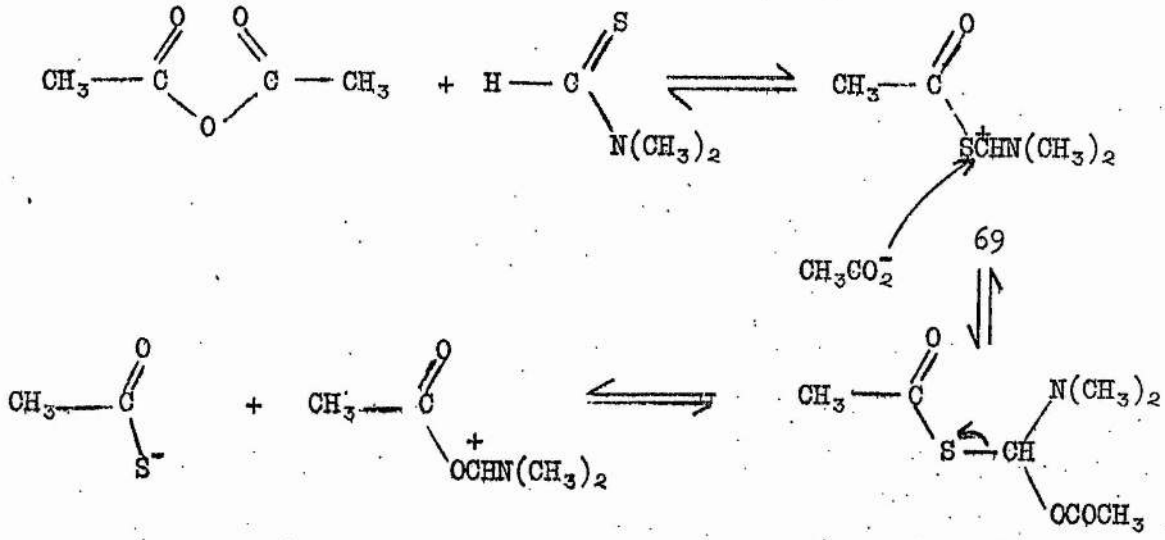


69

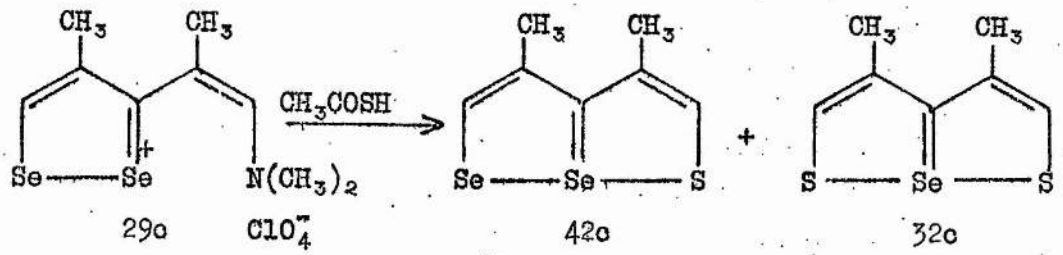
(67) and/or (68) was found. Subsequent solvolysis of the oil containing the cation (29b) with group VI nucleophiles afforded only low (ca. 10%) yields of the products. It is therefore concluded that self-condensation of 3-methyl-5-phenyl-1,2-diselenolium perchlorate (28b), rather than condensation with dimethylthioformamide, is the major reaction, and the products of the self-condensation decompose under the conditions used for condensation.

Both 3-ethyl-4-methyl-1,2-diselenolium perchlorate (28c) and 3-(2-dimethylamino-1-methylvinyl)-4-methyl-1,2-diselenolium perchlorate (29c) gave 3,4-dimethyl-1,6-dithia-6a-selenapentalene (32c) (scheme 28) in identical yields when boiled with dimethylthioformamide in acetic anhydride for thirty minutes. Dimethylthioformamide in acetic anhydride forms an electrophilic reagent (69) and it is difficult to envisage how this could react with the salt (29c). However, it is possible that thiolacetate ion is formed (scheme 29) in the reaction mixture which might then react with the salt (29c) affording 3,4-dimethyl-1,6-dithia-6a-selenapentalene (32c) via 3,4-dimethyl-1-thia-6,6a-diselenapentalene (42c). 3-(2-Dimethylamino-1-methylvinyl)-4-methyl-1,2-diselenolium perchlorate (29c) gave (scheme 30) a 1:1 mixture of the analogues (32c) and (42c) when boiled with thiolacetic acid whereas 3,4-dimethyl-1,6,6a-triselenapentalene (41c) afforded the 1,6-dithia analogue (32c) in high yield. Only a small yield of mixed analogues was obtained, however, by boiling the triselenapentalene (41c) with dimethylthioformamide in acetic anhydride. Behringer[159] synthesised 2,5-dimethyl-6a-thiathiophthene in 9% yield by heating acetylacetone at 100°C in thiolacetic acid containing sodium acetate. Considerably better yields of 6a-thiathiophthenes (71) were obtained from the 1-phenyl-but-1-yne-3-ones (70) using similar reaction conditions.

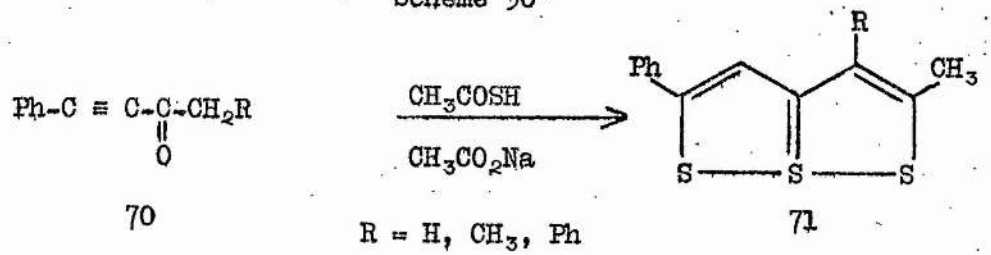
Tris (2-selenoformylcyclohexane-1-selenato) iron (III) (20d) afforded (scheme 31) 4,5-dihydro-3H-benzo[c,d]1-thia-6,6a-diselenapentalene



Scheme 29



Scheme 30



Scheme 31

(42d) when boiled for three hours with dimethylthioformamide in acetic anhydride and, with phosphoryl chloride and dimethylthioformamide, the 1,6-dithia-6a-selenapentalene (32d) was obtained. These condensation reactions demonstrate the similarity of the tris (1,3-diselenato) iron (III) complexes (20) to the 1,2-diselenolium perchlorates (28).

CHAPTER II

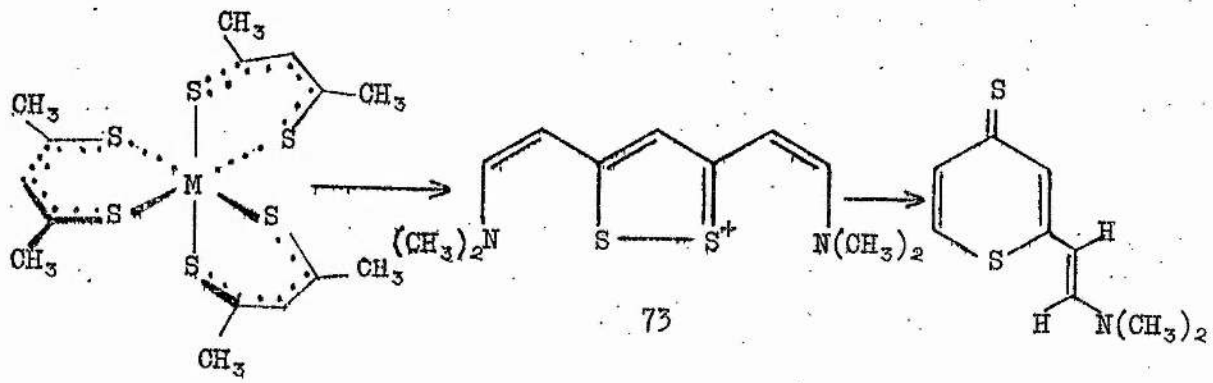
The Structures of Selenium Analogues of 6a-Thiathiophthenes and Related Compounds.

(1) Bis(1,2-Diselenolium)Tetrachloroferrates (II) (18).

It was found impossible to obtain N.M.R. spectra for the bis(1,2-diselenolium)tetrachloroferrates (II) (18) because of extensive line broadening, thus indicating the presence of unpaired electrons. Conversion of the bis(1,2-diselenolium)tetrachloroferrates (II) (18) into the corresponding 1,2-diselenolium perchlorates (28), for which satisfactory N.M.R. spectra were obtained, demonstrates, however, the presence of the 1,2-diselenolium cation in the bis(1,2-diselenolium) tetrachloroferrates (II) (18).

(2) Tris (1,3-Diselenato) Iron (III) Complexes (20).

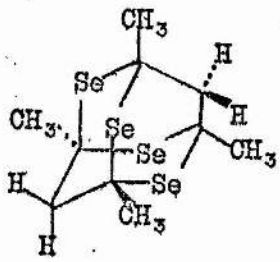
Unequivocal evidence for the formulation of compounds (20) as tris(1,3-diselenato) iron (III) complexes was found very difficult to obtain. No N.M.R. spectra could be obtained because of extensive line broadening and thermal decomposition prevented the observation of molecular ion peaks in their mass spectra. Both compounds (20) were insoluble in water, unlike the bis(1,2-diselenolium) tetrachloroferrates (II) (18), and they did not react with perchloric acid. Microanalyses showed the compounds (20) to be of formula $(\text{ligand})_3$ Fe. The physical characteristics and method of preparation of the compounds (20) are very similar to those of the tris(4-thiolopent-3-ene-2-thione) complexes of iron (III), ruthenium (III), and osmium (III) (72) prepared by Heath and Martin.[113] Thus, they are relatively stable to air and moisture, sparingly soluble in organic solvents giving intense brown solutions, difficult to recrystallise, and they decompose on heating.



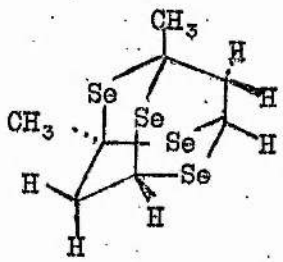
72 73 74

M = Fe, Ru, Os

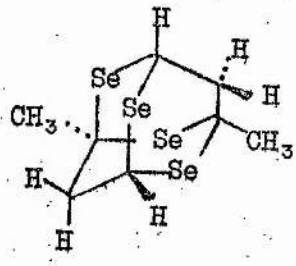
Scheme 32



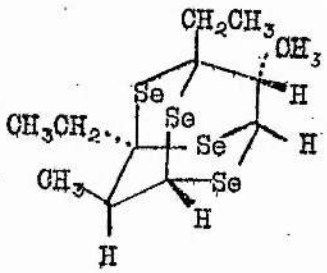
19a



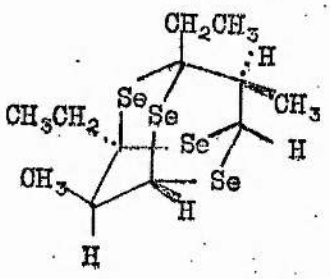
19e,i



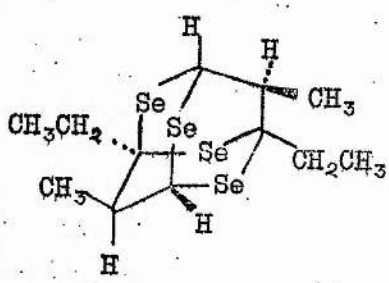
19e,ii



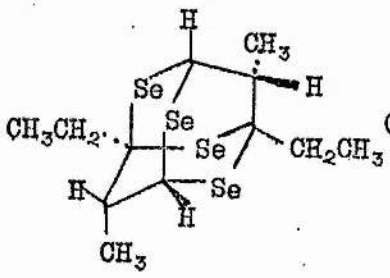
19c,i



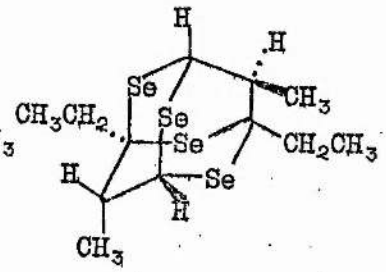
19c,ii



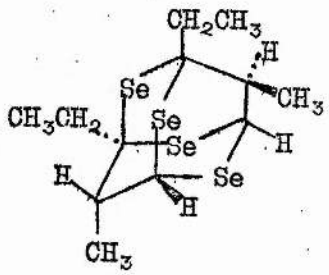
19c,iii



19c,iv



19c,v

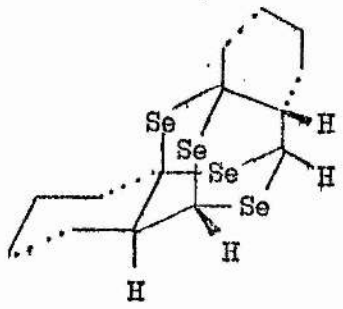


19c,vi

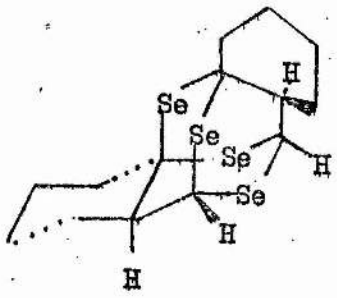
Probably the most convincing evidence, however, for their formulation as tris(1,3-diselenato) iron (III) complexes lies in their reactivity. On heating with phosphoryl chloride and dimethylthioformamide, red oils assumed to contain the cations (29) were obtained (scheme 2), which reacted with group (VI) nucleophiles affording analogues of 6a-thiathiophthenes. Under the same conditions, tris(4-thiolopent-3-ene-2-thione) iron (III) (72,M=Fe) has been shown to react with phosphoryl chloride and dimethylthioformamide giving a red oil which, with sodium hydrogen sulphide, afforded (scheme 32) 2-(2'-dimethylaminovinyl)-4H-thiopyran-4-thione (74). It is considered that condensation of dimethylthioformamide with tris(4-thiolopent-3-ene-2-thione) iron (III) (72, M=Fe) occurs at both methyl groups giving the cation (73) which affords the thione (74) with aqueous sodium hydrogen sulphide. The mechanisms of both condensation and rearrangement reactions are, as yet, unknown. The structure of 2-(2'-dimethylaminovinyl)-4H-thiopyran-4-thione (74) rests on its N.M.R. spectrum (see Experimental Section) and on independant synthesis by condensation of dimethylthioformamide with 2-methyl-4H-thiopyran-4-thione. A trans-arrangement for the vinyl protons in the enamine (74) is indicated by the magnitude of the vinyl coupling constant (13.4 Hz).

(3) 2,4,6,8-Tetraselenaadamantanes (19).

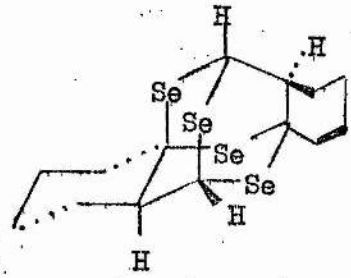
1,3,5,7-Tetramethyl-2,4,6,8-tetraselenaadamantane (19a) is a completely symmetrical molecule, as reflected by its N.M.R. spectrum which shows two sharp singlets, and its sharp melting point. Molecular models indicate that 1,3-dimethyl-2,4,6,8-tetraselenaadamantane (19e) exists as optical isomers (19e, i) and (19e, ii), and also the protons of the methylene groups at C-9 and C-10 are



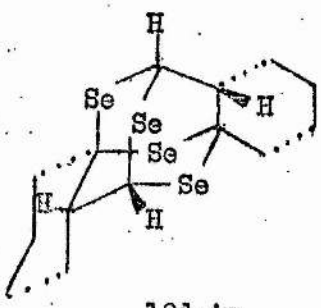
19d,i



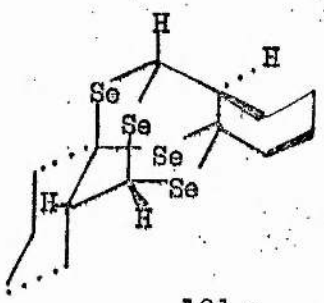
19d,ii



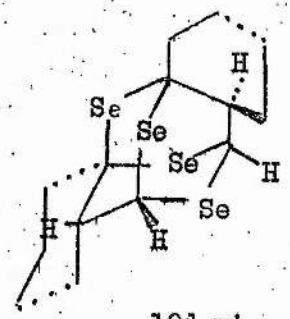
19d,iii



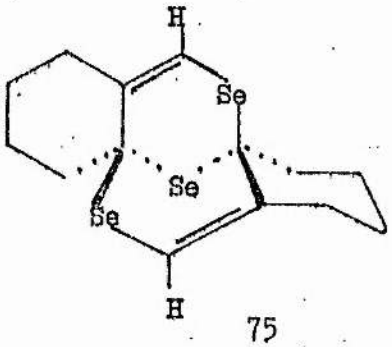
19d,iv



19d,v



19d,vi



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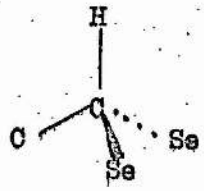

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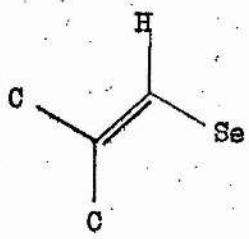

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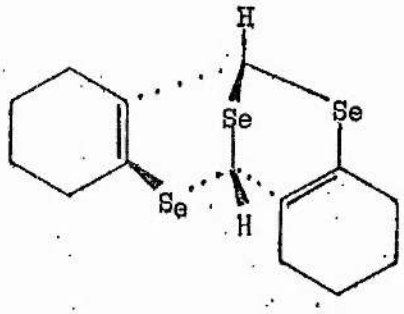
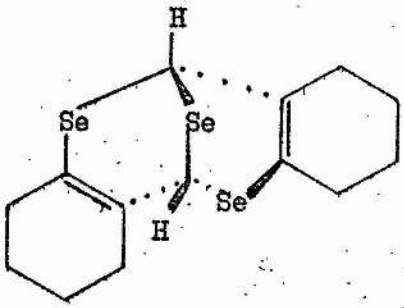
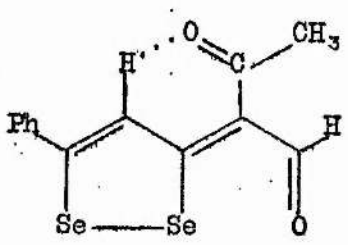


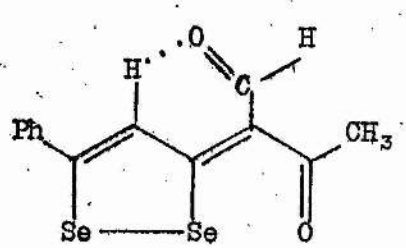
21a



21b



35f,i



35f, ii

non-equivalent. The double doublet expected for the methylene groups in the N.M.R. spectrum is not fully resolved, the peaks merging into a broad triplet. The melting point of 1,3-diethyl-9,10-dimethyl-2,4,6,8-tetraselenaadamantane (19c) covers a range of 37° and here models show the possibility of three geometrical isomers (19c, i), (19c, ii), and (19c, iii) each with an optical isomer (19c, iv), (19c, v) and (19c, vi). Sharp signals are observed, however, in the N.M.R. spectrum for the two pairs of methyl groups and the methylene groups but the signals for the pairs of protons at C-5, C-7 and C-9, C-10 are broad multiplets. Three geometrical isomers (19d, i), (19d, ii), and (19d, iii) each with an optical isomer (19d, iv), (19d, v), and (19d, vi) are possible for the similarly substituted bis(1,9;3,10)-cyclohexano-2,4,6,8-tetraselenaadamantane (19d). The sharp melting point, however, and sharp singlet in the N.M.R. spectrum for the pair of protons at C-5, C-7 indicate that only one geometrical isomer is formed.

In the reaction between 2-hydroxymethylene cyclohexanone (17d) and hydrogen selenide in ethanolic hydrogen chloride containing iron (III) chloride, a second neutral compound was isolated and formulated as 2,10,17-triselenatetracyclo[7,7,1,$O^{3,8}$,$O^{11,16}$] heptadeca-$\triangle^{3,8}$, $\triangle^{11,16}$-diene (21) rather than the isomeric 8,16, 17-triselenatetracyclo[7,7,1,$O^{1,6}$,$O^{9,14}$]heptadeca-$\triangle^{6,7}$,$\triangle^{14,15}$-diene (75) on the basis of its N.M.R. spectrum. The spectrum shows a sharp two proton singlet at δ 4,65 in accord with two protons in the environment (76) and not in the environment (77) for which a value of ca.δ 6.0 would be expected. Two distinct groups of ring protons are observed at δ 1.6-2.0 and δ 2.1-2.5 attributed to the [5 + 6 + 13 + 14] and the [4 + 7 + 12 + 15] methylene groups in

structure (21). 2,10,17-Triselenatetracyclo[7,7,1,$O^{3,8}$,$O^{11,16}$] heptadeca-$\triangle^{3,8}$,$\triangle^{11,16}$-diene also exists as optical isomers (21a) and (21b).

(4) 3-(2-Dimethylaminovinyl)-1,2-Diselenolium Salts (29).

The red oils obtained by condensation of the 1,2-diselenolium perchlorates (28a) and (28b) with dimethylthioformamide were assumed to contain the cations (29a) and (29b) by analogy with the similar condensation of 1,2-dithiolium salts (9) which afforded[24,25] crystalline salts (10). In one case, however, a crystalline salt, 3-(2-dimethylamino-1-methylvinyl)-4-methyl-1,2-diselenolium perchlorate (29c) was obtained and characterised. Condensation of the tris(1,3-diselenato) iron (III) complexes (20) with dimethylthioformamide also afforded red oils which were assumed to contain the cations (29d) and (29e) (scheme 2) in view of their reactivity with group (VI) nucleophiles.

(5) 3-Acylmethylene-3H-1,2-Diselenoles (35).

A comparison of the N.M.R. spectra of 3-acylmethylene-3H-1,2-diselenoles (31) and (35) with those of the corresponding 3-acylmethylene-3H-1,2-dithioles (12)[15,18,24] shows that replacement of the sulphur atoms by selenium brings about a downfield shift of ring and substituent proton signals. This effect is most marked in the 1,2-diselenole ring where proton signals for H-5 are shifted downfield by 0.8-1.0 p.p.m. and signals for H-4 are shifted downfield by 0.7-0.8 p.p.m.. Ring methyl signals are shifted downfield by ca. 0.1 p.p.m.. The effect on the formyl protons is less marked, there being a downfield shift of 0.05-0.1 p.p.m.. The N.M.R. spectrum of 3-(1-formyl-1-acetylmethylene)-5-phenyl-3H-1,2-diselenole (35f) exhibits two methyl signals at δ 2.52 and δ 2.59 and four proton signals at δ 10.00, δ 10.10, δ 10.20, and δ 10.29 as well as a phenyl multiplet.

From the intensity of the peaks, the signals can be divided into two groups comprising the signals at δ 2.52, δ 10.00, and δ 10.29 and those at δ 2.59, δ 10.10, and δ 10.20 in the ratio 1:6, indicating that 3-(1-formyl-1-acetylmethylene)-5-phenyl-3H-1,2-diselenole (35f) is formed as a mixture of cis and trans isomers (35f, i) and (35f, ii). Tentatively, the signals at δ 10.20 and δ 10.29 are assigned to the formyl protons and the signals at δ 10.00 and δ 10.10 to the protons at the 4-position of the 1,2-diselenole ring. The strong deshielding (1,86 p.p.m.) of the proton in the 4-position when compared with the corresponding proton of 3-formylmethylene-5-phenyl-3H-1,2-diselenole (35b) suggests that the formyl or acetyl group trans to the 1,2-diselenole ring has a preferred conformation with the oxygen atom held in close proximity to H-4, (35f, i) and (35f, ii).

The I.R. spectra of the 3-acylmethylene-3H-1,2-diselenoles (31) and (35) are characterised by a band of medium intensity situated between 1530 cm^{-1} and 1575 cm^{-1} which is assigned to the carbonyl stretching frequency. These values are similar to those found for the 3-acylmethylene-3H-1,2-dithioles by Lozac'h and his colleagues.[56,75] The dicarbonyl compound (35f) shows an intense band at 1648 cm^{-1} attributed to the trans carbonyl group and a second band of medium intensity at 1511 cm^{-1} attributed to the carbonyl group cis to the 1,2-diselenole ring.

The ultra-violet and visible spectra of the 3-acylmethylene-3H-1,2-diselenoles (31) and (35) also show a strong resemblance to the spectra[15,18,24] of the corresponding sulphur analogues. Thus, the spectra exhibit two main absorption bands, one situated between 223-233 nm and the second, responsible for their yellow colour, situated between 446-469 nm. The position and intensity of the lower

wavelength band is identical to that found for the 3-acylmethylene-3H-1,2-dithioles (12). Replacement of the sulphur atoms by selenium causes, however, a shift (18-29 nm) of the visible absorption to longer wavelength, the extinction coefficient remaining unaltered.

The similarity shown between the spectral data of the 3-acylmethylene-3H-1,2-diselenoles (35) and the corresponding sulphur analogues (12) reflects the structural similarity of the two systems. The structure of the 3-acylmethylene-3H-1,2-diselenoles (31) and (35) can therefore be regarded in terms of the limiting forms (78), (79), and (80). A considerable contribution from the polarised form (79) is envisaged in view of the low stretching frequency of the carbonyl absorption in their infra-red spectra. It is more difficult, however, to assess a contribution from the covalent form (80) since the dipole moments for the 3-acylmethylene-3H-1,2-diselenoles (35) and the selenium-oxygen distances have not been measured. A contribution is expected from the bicyclic structure (80) since selenium-oxygen bonding has been shown to occur by the isolation of 3,4-dimethyl-1,6-dioxa-6a-selenapentalene (48).

(6) 1-Thia-6,6a-Diselenapentalenes (42).

When the N.M.R. spectra of the 1-thia-6,6a-diselenapentalenes (42) are compared with those of the corresponding 6a-thiathiophthenes (4),[15,24,28] it is revealed that the selenium atoms cause a strong deshielding effect, bringing about a downfield shift of ring and substituent proton signals. Thus, $\Delta\delta$ for the 2-, 3-, 4-, and 5-proton signals of 1-thia-6,6a-diselenapentalene (42e) are 0.24, 0.36, 0.60, and 1.14 p.p.m. respectively when compared with the corresponding proton signals of 6a-thiathiophthene. Similar values for $\Delta\delta$ are found for ring protons in substituted 1-thia-6,6a-diselenapentalenes (42) when compared with the corresponding 6a-thiathiophthenes. Ring methyl groups of substituted 1-thia-

6,6a-diselenapentalenes (42a), (42c), and (42g) are deshielded by 0.03 - 0.14 p.p.m., the stronger deshielding occurring at the 3- and 4-positions (42c), when compared with the corresponding 6a-thiathiophthenes. The coupling constants of 1-thia-6,6a-diselenapentalene (42e) are found to be 7.1 Hz for the AB system of the 1,2-diselenole ring and 6.5 Hz for the AB system of the 1,2-thiaselenole ring, compared to a value of 6.3 Hz for the AB system in 6a-thiathiophthene.[24]

Reaction of the cation (29f) with aqueous sodium hydrogen sulphide afforded 3-acetyl-5-phenyl-1-thia-6,6a-diselenapentalene (42f) rather than the isomeric 3-(1-acetyl-1-thioformylmethylene)-5-phenyl-3H-1,2-diselenole (81) implying that the bicyclic 1-thia-6,6a-diselenapentalene system (42f) is more energetically favoured than the 3-acylmethylene-3H-1,2-diselenole (81). The N.M.R. spectrum of 3-acetyl-5-phenyl-1-thia-6,6a-diselenapentalene (42f) shows two low field singlets at δ 10.11 and δ 10.38, assigned to H-4 and H-2 respectively. Protons -2 and -4 of 3-acetyl-5-phenyl-1-thia-6,6a-diselenapentalene (42f) are deshielded by 1.00 p.p.m. and 1.35 p.p.m. respectively when compared with the corresponding proton signals of 5-phenyl-1-thia-6,6a-diselenapentalene (42b) as a result of the anisotropic and inductive effects of the carbonyl group. The absorption frequency of the carbonyl group (1664 cm^{-1}, $CHCl_3$) is similar to that of acetophenone (1689 cm^{-1}, liquid film).

The ultra-violet and visible spectra of 6a-thiathiophthenes[24] (4) are characterised by either a peak or shoulder situated at 230-236 nm (log ϵ 4.25) and a peak situated at 249-264 nm (log ϵ 4.65), with a further peak situated at 470-495 nm (log ϵ 3.75). When the 1- and 6a-sulphur atoms are replaced by selenium, further peaks are introduced at 203-215 nm (log ϵ 4.36) and at 315-323 nm (log ϵ 3.50). The peak or shoulder present at 230-236 nm in 6a-thiathiophthenes (4) is shifted to longer wavelength by 8-10 nm

with a slight increase in intensity, whereas the peak at 249-264 nm is not influenced. The most characteristic difference, however, lies in the visible region of 1-thia-6,6a-diselenapentalenes where the peak present at 470-495 nm in 6a-thiathiophthenes is now shifted to longer wavelength by 19-27 nm and a shoulder is introduced at 542-584 nm (log ϵ 3.12).

No data of bond distances are available for the 1-thia-6,6a-diselenapentalenes (42) and hence the effect on the bond distances of replacing the 1- and 6a-sulphur atoms of 6a-thiathiophthenes (4) by selenium cannot be ascertained. However, the similarity of their electronic and N.M.R. spectra suggest that the same type of bonding is present in 1-thia-6,6a-diselenapentalenes (42) as in 6a-thiathiophthenes (4). Therefore, the 1-thia-6,6a-diselenapentalenes are best formulated as bicyclic systems (42) having a selenium-selenium-sulphur bonding sequence.

(7) 1,6,6a-Triselenapentalenes (41).

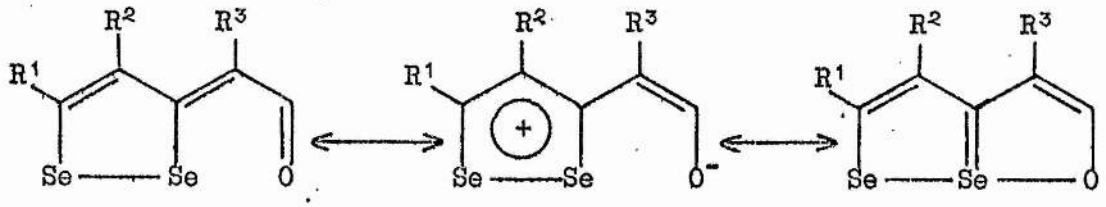
A comparison of the N.M.R. spectra of 1,6,6a-triselenapentalenes (41) with those of the corresponding 6a-thiathiophthenes[24] (4) shows that replacement of the three sulphur atoms in 6a-thiathiophthenes (4) by selenium brings about a downfield shift of ring proton signals. Protons at the 2- and 5-positions are deshielded by 1.17-1.38 p.p.m. whereas protons at the 3- and 4-positions are deshielded by 0.58-0.72 p.p.m.. The methyl groups of 3,4-dimethyl-1,6,6a-triselenapentalene (41c) are deshielded by 0.15 p.p.m. but that of 2-methyl-1,6,6a-triselenapentalene (41a) is shielded by 0.07 p.p.m. when compared with the corresponding 6a-thiathiophthenes. The N.M.R. spectrum of 1,6,6a-triselenapentalene (41e) in deuteriochloroform shows one AB pair of doublets at δ 8.65 and δ 10.41 (J = 6.9 Hz), which have been assigned to the 3- and 4-protons and the 2- and 5-protons respectively. Protons in the 2- and 5-positions of 1,6,6a-triselenapentalenes

(41) are found to absorb between δ 10.07 and δ 10.41, and protons in the 3- and 4-positions absorb between δ 8.43 and δ 8.84. Spectra of symmetrically substituted 1,6,6a-triselenapentalenes (41c), (41d), and (41e) show magnetic equivalence of ring protons or identical substituents at the pairs of sites C-2, C-5 and C-3, C-4. This demonstrates that these compounds, in solution, possess real or time-averaged C_{2v} symmetry.

The N.M.R. spectrum of 2-phenyl-4-acetyl-1,6,6a-triselenapentalene (41f) exhibits singlets at δ 10.17 and δ 11.08 which have been assigned to H-3 and H-5 respectively. H-3 of 2-phenyl-4-acetyl-1,6,6a-triselenapentalene (41f) is deshielded by 1.33 p.p.m. compared with the corresponding proton of 2-phenyl-1,6,6a-triselenapentalene (41b). This deshielding is identical to that of H-4 of 3-acetyl-5-phenyl-1-thia-6,6a-diselenapentalene (42f) when compared with the corresponding proton of 5-phenyl-1-thia-6,6a-diselenapentalene (42b).

The band present at 249-264 nm in the electronic spectra of 6a-thiathiophthenes (4) is shifted to longer wavelength by 11-18 nm to 267-281 nm when the three sulphur atoms are replaced by selenium. The extinction coefficient of this band remains almost unaltered. In the visible region, the band exhibited by 6a-thiathiophthenes (4) at 470-492 nm is shifted by 53-59 nm to longer wavelength in the spectra of 1,6,6a-triselenapentalenes (41) to 524-546 nm, also with a closely similar extinction coefficient. The shoulder observed at 542-584 nm in the electronic spectra of 1-thia-6,6a-diselenapentalenes (42) is now shifted to longer wavelength by 59-75 nm becoming a discrete band at 622-664 nm with an extinction coefficient of ca, 2.90. Solutions of 1,6,6a-triselenapentalenes (41) are thus a rich blue colour through which a red colour can be seen.

The crystal and molecular structure of 1,6,6a-triselenapentalene



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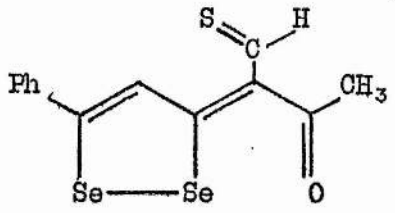

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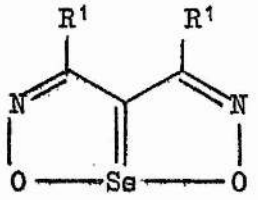

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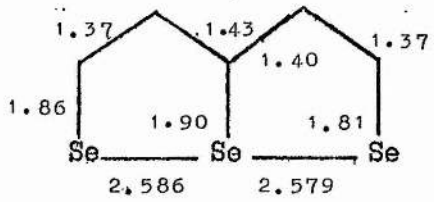


Fig.1

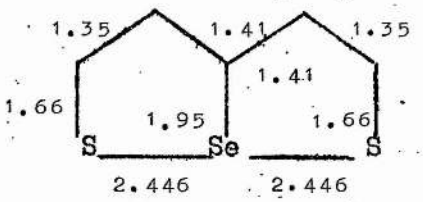


Fig.2

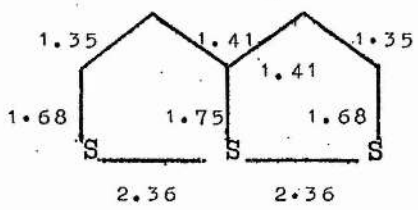


Fig.3

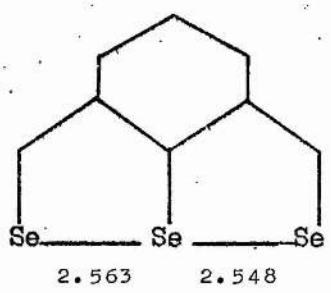
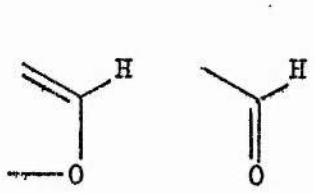


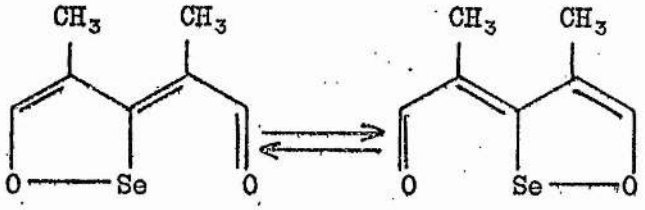
Fig.4

	Se_1-Se_2 A°	Se_2-Se_3 A°
$K(SeCN)_3.1/2\ H_2O$	2.69	2.65
$Rb(SeCN)_3.1/2\ H_2O$	2.66	2.66
$Cs(SeCN)_3$	2.65	2.65
$[SeC(NH_2)_2]_3Cl_2.H_2O$	2.60	2.72
$[SeC(NH_2)_2]_3Br_2.H_2O$	2.62	2.71

Table 1



83 84



85 86

has been determined by Hordvik.[156,160] The molecule (fig. 1) is planar and the almost equivalent selenium-selenium bonds (2.586 A^{o} and 2.579 A^{o}) are 0.24 A^{o} (10.7%) longer than a selenium-selenium single covalent bond.[71] By comparison, the selenium-sulphur bonds in 1,6-dithia-6a-selenapentalene (fig. 2)[156] are 10.1% longer than the sum of the covalent radii of selenium and sulphur, and the sulphur-sulphur bonds in 6a-thiathiophthene (fig. 3)[156] are 12.4% longer than the sulphur-sulphur single bond in a cis planar disulphide group.[31] Also, the terminal (1.37 A^{o}) and central (1.43 A^{o} and 1.40 A^{o}) carbon-carbon bonds of 1,6,6a-triselenapentalene (fig. 1) are very similar to the lengths of the corresponding bonds in 1,6-dithia-6a-selenapentalene (fig. 2) and 6a-thiathiophthene (fig. 3). In crystals of 1,6,6a-triselenapentalene, several intermolecular atomic distances are shorter than the corresponding van der Waals distances; they are: Se(1) ...H (5')' = 3.08 A^{o}, Se(1) ... Se(6)' = 3.92 A^{o}, Se(6) ... Se(6)' = 3.87 A^{o}, Se(6a) ... Se(6a)' = 3.83 A^{o}, and Se(6) ... Se(1)' = 3.90 A^{o}; also Se (6a) lies only 3.55 A^{o} from the plane of its nearest molecule. It is also interesting to note that the environment of each of the three selenium atoms is roughly square planar. Equal selenium-selenium bond distances have also been found[161] in 4,5-dihydro-3H-benzo[cd]-1,6,6a-triselenapentalene (fig. 4).

Previous structure investigations of linear three-selenium systems have been carried out by Hauge on potassium triselenocyanate hemihydrate,[162] rubidium triselenocyanate hemihydrate,[163] cesium triselenocyanate,[163] triselenourea dichloride hydrate,[164] and triselenourea dibromide hydrate.[164] The sum of the selenium-selenium bond lengths in these salts (table 1) ranges from 5.30 A^{o} to 5.34 A^{o}, and the average selenium-selenium bond length is 2.66 A^{o}, as compared with a normal selenium-selenium single covalent bond length of 2.34 A^{o}.[71] The bonding between the three linear selenium

atoms may be regarded as a system using three orbitals occupied by four electrons, analogous to the bonding in the interhalogen compounds.[64]

The N.M.R. spectrum of 1,6,6a-triselenapentalene (41e) shows that in solution the molecule is symmetrical. In the crystalline state, 1,6,6a-triselenapentalene (fig. 1) is almost symmetric about a plane perpendicular to the molecular plane, and passing through selenium (6a) and carbon (3a). The deviation from a symmetrical structure in the crystal may be attributed to intermolecular forces. 1,6,6a-Triselenapentalene (41e) thus exhibits a similar pattern to that shown by 6a-thiathiophthenes (4), 1,6-dithia-6a-selenapentalenes (7), isothiazolo [5,1-e] isothiazoles (6), and [1,2,5] oxaselenazolo [2,3-b][1,2,5] oxaselenazoles-7-Se^{IV} (82) and is therefore represented by a bicyclic formulation (41e) having a linear selenium-selenium-selenium bonding sequence rather than a rapid valence isomerisation (2) $\rightleftharpoons$ (3) (A = B = C = Se).

The bonding in 1,6,6a-triselenapentalene (41e) may be regarded as analogous to that proposed by Gleiter and Hoffmann[52] for 6a-thiathiophthene. Thus, the three selenium atoms may be considered as a linear system using three orbitals occupied by four electrons for σ bonding with π bonding superimposed by the delocalised 10 π electron system. The average length of the selenium-selenium bonds in 1,6,6a-triselenapentalene (2.58 Å) is 0.08 Å shorter than the average selenium-selenium bond length (2.66 Å) in the triselenocyanate and triselenourea ions (table 1) which have no π bonding superimposed on the three-centre four-electron bond.

(8) 1,6-Dithia-6a-Selenapentalenes (32).

The structure of the 1,6-dithia-6a-selenapentalenes (32) (6a-selenathiophthenes), initially prepared by Reid,[99] has previously been discussed (Part I, Chapter V, 7). 4,5-Dihydro-3H-benzo[c,d]-1,6-dithia-6a-selenapentalene (32d), the only new member of this

series synthesised, shows similar spectral properties to those of analogues already published. Thus, its N.M.R. spectrum exhibits a singlet at δ 9.05 (2 + 6 - H), a triplet at δ 3.05 (3 + 5 - CH_2), and a quintet at δ 2.00 (4 - CH_2) demonstrating that in solution the molecule is symmetrical. The chemical shifts for the protons of 4,5-dihydro-3H-benzo[c,d]-1,6-dithia-6a-selenapentalene (32d) are shifted only slightly downfield when compared with the chemical shifts for corresponding protons of the analogous 6a-thiathiophthene (89d). Protons-2 and -6 are shifted downfield by 0.27 p.p.m.. The electronic spectra of 1,6-dithia-6a-selenapentalenes (32) also show only minor differences from the spectra of the corresponding 6a-thiathiophthenes (4). Thus, the band present at 249-264 nm in the ultra-violet spectra of 6a-thiathiophthenes (4) is shifted to longer wavelength by 4-7 nm, and the band at 470-492 nm is shifted to longer wavelength by 1-11 nm in the 1,6-dithia-6a-selenapentalenes (32). The close similarity of the electronic spectra of the 6a-thiathiophthenes (4) with those of the 1,6-dithia-6a-selenapentalenes (32) demonstrates the similarity of the bonding in the two systems.

The recent structure study[156] of 1,6-dithia-6a-selenapentalene (fig. 2), showing equal sulphur-selenium bonds (2.446 Å), and the magnetic equivalence of ring protons or identical substituents at the pairs of sites C-2, C-5 and C-3, C-4 in the N.M.R. spectra of 1,6-dithia-6a-selenapentalenes (7),[99] confirms their formulation as bicyclic systems (7) rather than a rapid valence isomerisation (2) $\rightleftharpoons$ (3) (A, C = S; B = Se).

(9) 3,4-Dimethyl-1,6-Dioxa-6a-Selenapentalene (48).

A pale yellow compound, isolated in low yield from the reaction between 3-(2-dimethylamino-1-methylvinyl)-4-methyl-1,2-diselenolium perchlorate (29c) and aqueous sodium hydrogen selenide (scheme 17), is formulated as 3,4-dimethyl-1,6-dioxa-6a-selenapentalene (48) on the

basis of spectral data and its reaction with phosphorus pentasulphide.

High resolution mass spectrometry established the molecular formula as $C_7H_8SeO_2$ rather than the formula C_7H_8SeS of similar molecular weight. The mass spectrum also showed a peak at m/e^+ 176 corresponding to loss of carbon monoxide from the parent molecular inn (m/e^+ 204) with a meta-stable peak at m/e^+ 151.8 corresponding to that transition.

The N.M.R. spectrum exhibits two sharp singlets at δ 2.47 and δ 8.62 in the ratio 3:1, demonstrating that the compound is symmetrical in solution. Moreover, the chemical shift of H-2 + H-5 in 3,4-dimethyl-1,6,6a-triselenapentalene (41c) is δ 10.21 and that of the corresponding protons in 3,4-dimethyl-1,6-dithia-6a-selenapentalene (32c) is δ 9.20. Therefore, a chemical shift of δ 8.62 would not be unexpected for protons in the 2- and 5-positions of 3,4-dimethyl-1,6-dioxa-6a-selenapentalene (48), A comparison of the N.M.R. spectrum with that of 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole (35c), in which the chemical shift of the formyl proton is δ 9.27, also suggests protons in the environment (83) rather than the environment (84).

The infra-red spectrum shows a doublet of medium intensity at 1526 cm^{-1} and 1543 cm^{-1} which is the only peak situated between 1500 cm^{-1} and 2900 cm^{-1}. 3-(1-Formylethylidene)-4-methyl-3H-1,2-diselenole (35c) exhibits a peak at 1564 cm^{-1} attributed to the carbonyl stretching frequency.

The ultra-violet spectrum shows four bands, that at longest wavelength (381 nm) and greatest intensity being responsible for the pale yellow colour of the compound.

The N.M.R. and infra-red spectra are in accord with its formulation as 3,4-dimethyl-1,6-dioxa-6a-selenapentalene (48). Reaction of this compound with phosphorus pentasulphide afforded 3,4-dimethyl-1,6-dithia-6a-selenapentalene (32c) thus providing conclusive evidence for

this formulation. By analogy with 6a-thiathiophthenes (4), 1,6-dithia-6a-selenapentalenes (7), 1,6,6a-triselenapentalenes (41), isothiazolo [5,1-e]isothiazoles (6), and [1,2,5]oxaselenazolo [2,3-b][1,2,5] oxaselenazoles-7-Se^{IV} (82), a bicyclic formulation (48) containing oxygen-selenium bonds is proposed for 3,4-dimethyl-1,6-dioxa-6a-selenapentalene rather than a system of valence isomers (85) ⟷ (86).

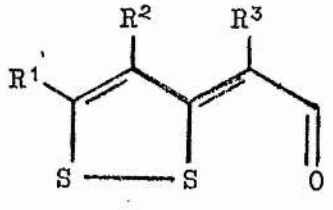
CHAPTER III

The Rearrangement of 6a-Thiathiophthenes (89) and 3-Acylmethylene-3H-1,2-Dithioles (87) by Nucleophiles

(1) The Rearrangement of 3-Acylmethylene-3H-1,2-Dithioles (87) by Aqueous Sodium Hydrogen Sulphide.

The 3-acylmethylene-3H-1,2-dithioles (87 a-c) have been shown to rearrange with sodium hydrogen sulphide giving the corresponding 4H-thiopyran-4-thiones (88). Under various conditions of temperature and time [see Experimental, section XI part (1)], only minor yields of the corresponding 6a-thiathiophthenes (89 a-c) were obtained, presumably by a simple carbonyl-type reaction. 3-Formyl-5,6-dihydro-4H-benzo[c][1,2] dithiole (87d), however, afforded increasing yields of 4,5-dihydro-3H-benzo[cd]-6a-thiathiophthene (89d) with increasing temperature. Since 3-formyl-5,6-dihydro-4H-benzo[c][1,2] dithiole (87d) cannot rearrange to a 4H-thiopyran-4-thione, the only possible reaction with hydrosulphide ion is a carbonyl-type reaction giving 6a-thiathiophthene (89d). Carbonyl reactions of this type are known to be accelerated by higher temperature. The increased yield of 4,5-dihydro-3H-benzo[cd]-6a-thiathiophthene (89d) in changing the solvent from dimethylformamide to a mixture of dimethylformamide and ethanol can be attributed to the decreased nucleophilicity of hydrosulphide anion in this solvent, thus resulting in a decrease in breakdown products.

The 6a-thiathiophthenes (89 a-c) cannot be intermediates in the rearrangement of the 3-acylmethylene-3H-1,2-dithioles (87a-c) to the corresponding thiones (88 a-c) since 4-methyl-2-phenyl-6a-thiathiophthene (89a) gave only a 5% yield of the corresponding thione (88a) under conditions in which the 3-(1-formylethylidene)-5-phenyl-3H-1,2-dithiole (87a) rearranged almost quantitatively. Similar experiments with



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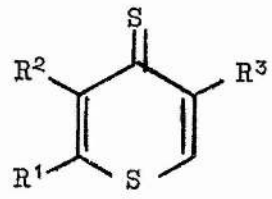

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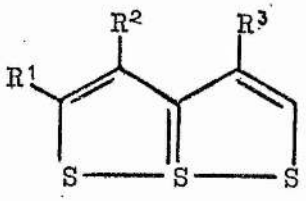
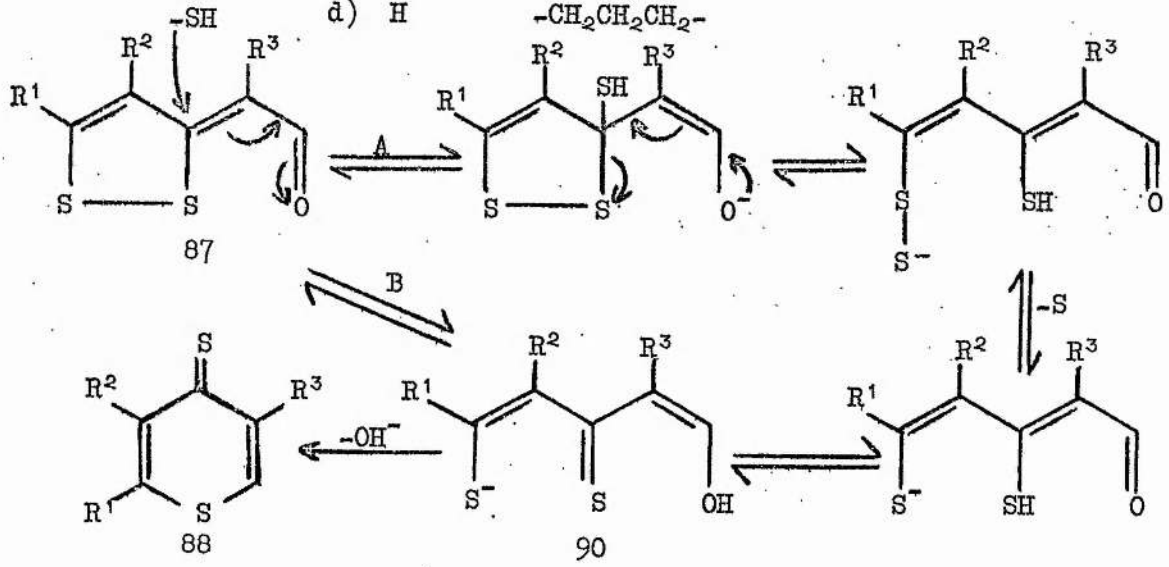
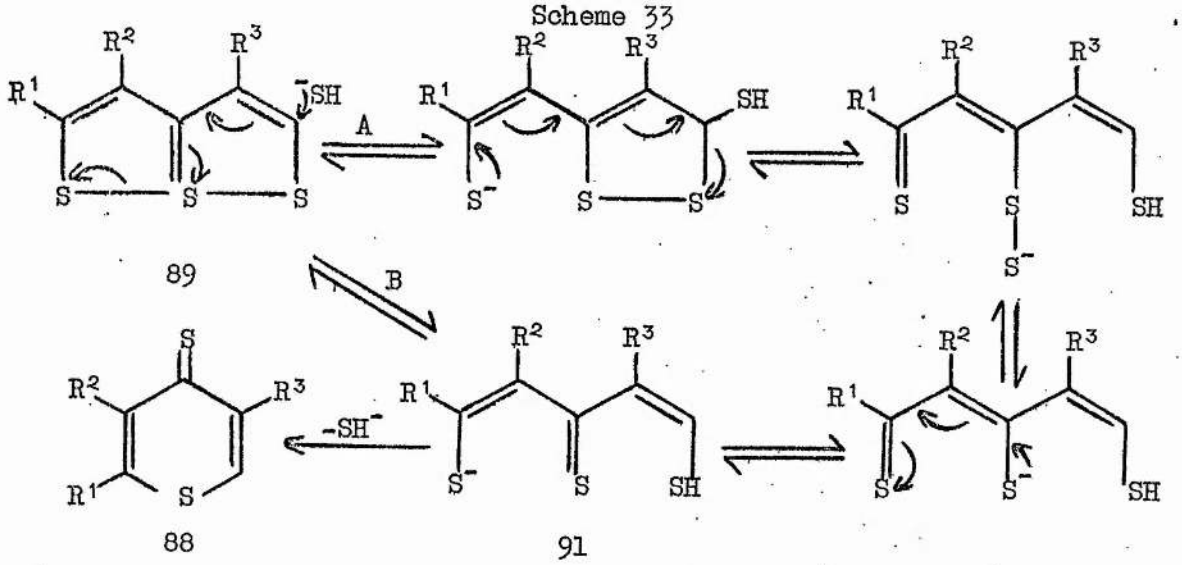


89

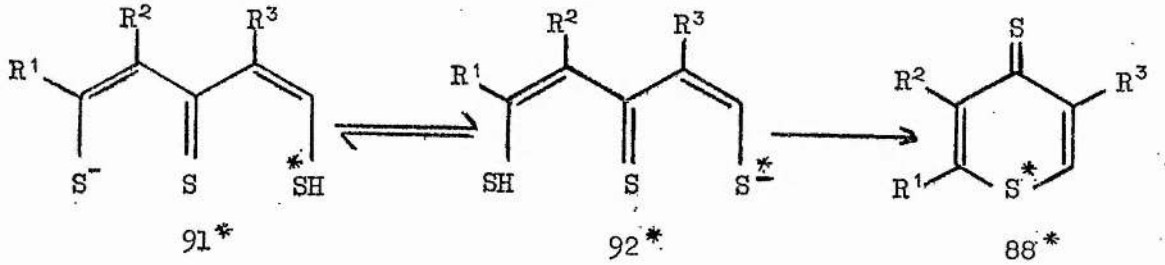
	R^1	R^2	R^3
a)	Ph_t	H	CH_3
b)	Bu^t	H	H
c)	Ph	H	H
d)	H	$-CH_2CH_2CH_2-$	



Scheme 33



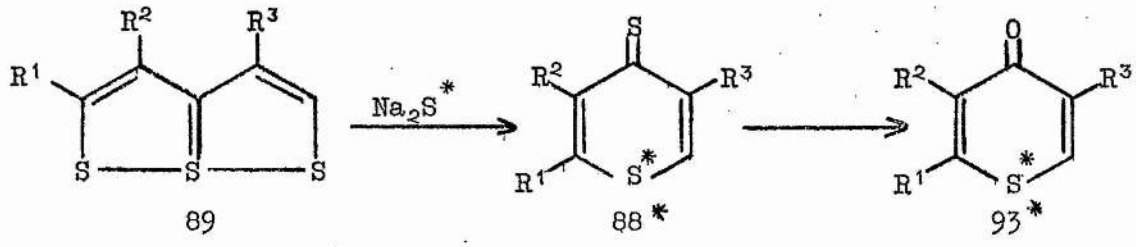
Scheme 34



2-t-butyl-6a-thiathiophthene (89b) and 2-phenyl-6a-thiathiophthene (89c) gave inconclusive evidence. Two mechanisms (scheme 33) are therefore possible for the rearrangement of 3-acylmethylene-3H-1,2-dithioles (87) to 4H-thiopyran-4-thiones (88). Nucleophilic attack (route A) by hydrosulphide ion at the 3-position of the 1,2-dithiole ring followed by loss of sulphur would afford the anion (90) which eliminates hydroxide ion on cyclisation to the 4H-thiopyran-4-thione (88). Alternatively, reductive cleavage of the sulphur-sulphur bond (route B) would give the same anion (90) directly, which cyclises similarly. These two mechanisms could be differentiated by the use of radio-labelled sodium hydrogen sulphide-S-35. Rearrangement by a nucleophilic mechanism (scheme 33, route A) would result in 100% introduction of radio-labelled sulphur into the thione group of the 4H-thiopyran-4-thione (88). Rearrangement by a reductive mechanism (scheme 33, route B) would, however, result in no incorporation of radio-labelled sulphur into the 4H-thiopyran-4-thione (88).

(2) The Mechanism of the Rearrangement of 6a-Thiathiophthenes (89) to 4H-Thiopyran-4-Thiones (88).

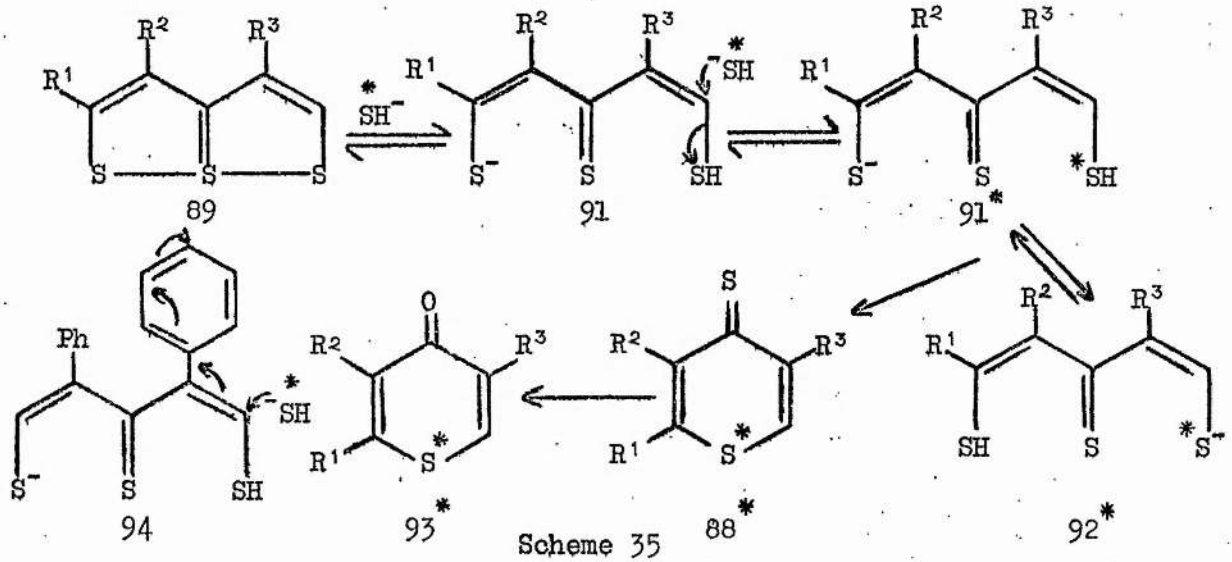
6a-Thiathiophthenes (89) were found[15,29] to rearrange with either aqueous sodium sulphide or sodium hydrogen sulphide to the corresponding 4H-thiopyran-4-thiones (88). Two mechanisms were proposed[15,29] for this rearrangement; a reductive cleavage of the sulphur-sulphur bond (scheme 34, route B) giving the intermediate anion (91) which eliminates hydrosulphide anion on cyclisation, or a nucleophilic attack (scheme 34, route A) by hydrosulphide anion at the 2- (or 5-) position of the 6a-thiathiophthene ring leading to the same anion (91) which then cyclises. The latter mechanism was favoured on the basis of substituent effects and since 2-phenyl-6a-thiathiophthene and 2,4-diphenyl-6a-thiathiophthene also rearranged



	R^1	R^2	R^3
a)	Ph, t-Bu	H	CH_3
b)	t-Bu	H	H
c)	Ph	H	H
e)	H	H	H
f)	H	CH_3	CH_3
g)	H	Ph	Ph

6a-Thia-thiophthene	Reaction Temperature	Reaction Time	4H-Thiopyran-4-one-S-35	% Incorporation of S-35	% Exchange at 6-position
89a	60	5 min.	93a	5.6	11.2
89b	60	5 min.	93b	14.6	29.2
89c	60	5 min.	93c	18.4	36.8
89e	60	5 min.	93e	55.3	55.3
89f	20	5 min.	93f	15.1	15.1
89g	20	ca.10 sec.	93g	77.0	77.0

Table 2



Scheme 35

with sodium hydroxide to the corresponding 4H-thiopyran-4-thiones.[29]

The two mechanisms have now been differentiated by the use of radio-labelled aqueous sodium sulphide-S-35. If the initial step in the rearrangement is a reductive cleavage of the sulphur-sulphur bond (scheme 34, route B), then ideally there would be no incorporation of labelled sulphur into the 4H-thiopyran-4-thione (88). An initial nucleophilic attack, however, by labelled sulphide (scheme 34, route A) would result in formation of the anion (91*) containing the label in the 6-position. On cyclisation, 50% of the label would be eliminated since the anion (91*) would be in equilibrium with its tautomer (92*). Therefore, if rearrangement proceeds by a nucleophilic mechanism, 50% of the original label would appear in the ring sulphur atom of the 4H-thiopyran-4-thione (88*).

In practise, it was found impossible to count radio-labelled 4H-thiopyran-4-thiones (88*) because of their strong colour quenching. The 4H-thiopyran-4-thiones (88*) were therefore converted into the colourless 4H-thiopyran-4-ones (93*) by the action of mercury (II) acetate in acetic acid and chloroform.[115] Quench calibration curves, relating the efficiency of counting to the external standard ratio of the scintillation counter, were prepared for each 4H-thiopyran-4-one (93) in order to calculate the efficiency of counting in each unknown sample. The percentage incorporation of sulphur-35 into the 4H-thiopyran-4-ones (93*), defined by the expression

$$\% \text{ incorporation} = \frac{\text{specific activity (4H-thiopyran-4-one)} \times 100}{\text{specific activity (sodium sulphide)}}$$

was calculated for the rearrangement of each of the 6a-thiathiophthenes (89a-g). These results are tabulated in table 2.

The data are consistent with an initial reductive cleavage of the sulphur-sulphur bond (scheme 34, route B) since a mechanism involving an initial nucleophilic attack (scheme 34, route A) would

result in a minimum of 50% incorporation of labelled sulphur into the 4H-thiopyran-4-one (93^*). The rearrangement of four of the 6a-thiathiophthenes (89) afforded 4H-thiopyran-4-ones (93^*) with less than 20% incorporation of labelled sulphur (table 2). However, the initially formed anion (91) is then susceptible to nucleophilic attack (scheme 35) at the unsubstituted sites (C-2 and/or C-5) leading to exchange of unlabelled sulphur for labelled sulphur from the reaction medium. The anion (91^*) $\rightleftharpoons$ (92^*) then cyclises eliminating 50% of the label incorporated by exchange. Exchange of both the 1- and 6-sulphur atoms is possible for the anions (91) derived from 6a-thiathiophthene (89e), 3,4-dimethyl-6a-thiathiophthene (89f), and 3,4-diphenyl-6a-thiathiophthene (89g). Therefore, both the 1- and 6- sulphur atoms in the anions (91e), (91f), and (91g) undergo 55.3%, 15.1%, and 77.0% exchange respectively. The substituent in the 2-position of 4-methyl-2-phenyl-6a-thiathiophthene (89a), 2-t-butyl-6a-thiathiophthene (89b), and 2-phenyl-6a-thiathiophthene (89c) effectively blocks this position so that only the 6-sulphur atom in the anions (91a), (91b), and (91c) can exchange with labelled sulphide from the surrounding medium. Thus, the 6-sulphur atom in the anions (91a), (91b), and (91c) undergoes 11.2%, 29.2%, and 36.8% exchange respectively. On cyclisation, 50% of this label is eliminated. A qualitative agreement with this mechanism is shown between the electronic effects of substituents and the percent exchange of the 6-sulphur atom in the anions (91) (scheme 35). The anion (91e) derived from 6a-thiathiophthene (89e) is taken as the reference with 55.3% exchange at the 6-sulphur atom. The positive inductive effect of a methyl substituent in the 4-position of the anion (91) is to increase the electron density at the 5-position. This position is therefore deactivated towards nucleophilic exchange when compared with the corresponding position of the anion (91e). The anions (91a) and (91f) derived from 4-methyl-2-phenyl-6a-thiathioph-

thene (89a) and 3,4-dimethyl-6a-thiathiophthene (89f) undergo only 11.2% and 15.1% exchange respectively at the 6-sulphur atom. A phenyl group in the 4-position withdraws electrons thus making the 5-position much more reactive towards nucleophilic exchange since the negative charge of the incoming labelled sulphide anion can be delocalised into the phenyl ring (94). Thus, the anion (91g) derived from 3,4-diphenyl-6a-thiathiophthene (89g) undergoes 77.0% exchange at the 6-sulphur atom under much milder conditions than was used for the rearrangement of other 6a-thiathiophthenes (89) (table 2).

PART THREE

EXPERIMENTAL

Introductory Notes

Melting points were determined on a Kofler hot-stage apparatus and are corrected.

Ultra-violet and visible spectra were measured with a Unicam SP800 spectrophotometer. Light absorption data refer to solutions in cyclohexane unless otherwise stated.

Infra-red spectra were measured with a Perkin-Elmer 257 spectrophotometer. Solutions were ca. 0.02 M in chloroform, carbon disulphide or carbon tetrachloride. ^{1}H N.M.R. spectra were measured at ca. 34° with a Perkin-Elmer R.10 spectrometer operating at 60 MHz and, where stated, at 31.5° with a Varian HA 100 spectrometer operating at 100 MHz. Chemical shifts (δ) are expressed in p.p.m. downfield from tetramethylsilane as internal reference. Solutions in trifluoroacetic acid (TFA) were 0.6 M and in deuteriochloroform ($CDCl_3$) and hexadeuteriodimethyl sulphoxide (d_6-DMSO) 0.5 M, except where these concentrations could not be attained, when saturated solutions were employed.

Mass spectra were obtained on an AEI MS 902 instrument. For compounds containing selenium, the peak quoted is the most intense peak in the multiplet. With one or two selenium atoms, this peak is that corresponding to selenium isotopes (1 x 80) and (2 x 80) respectively. For compounds containing three or four selenium atoms, the most intense peak is that corresponding to selenium isotopes (2 x 80 + 1 x 78) and (3 x 80 + 1 x 78) respectively.

Carbon, hydrogen and nitrogen microanalyses were carried out by Mr. J.R. Bews of this department. Selenium microanalysis was carried out by Dr. A. Bernhardt, Mulheim, Germany.

Thin-layer chromatography (T.L.C.) was on "Silica Gel G" plates which were developed in iodine vapour. Alumina for column chromatography was Spence Type H 100/200 mesh, and silica was Whatman "Chromedia" S.G.31.

Solutions were dried over anhydrous sodium sulphate. Solvents were evaporated at reduced pressure with a Büchi rotary film evaporator.

"Petrol" refers to 40/60 petroleum ether and "ether" to diethyl ether.

Acetic acid, acetic anhydride, acetone, chloroform, petrol, cyclohexane, dimethylformamide, ethanol, methanol, dimethylsulphoxide, chlorobenzene and thiolacetic acid were all redistilled commercial solvents.

Benzene for chromatography was dried by azeotropic distillation, the first twenty-five percent of the distillate being used for extractions.

Ether was allowed to stand over calcium chloride for 2 days, filtered and distilled.

Acetonitrile was boiled over sodium hydride (dispersion in oil, 2 grams per litre) for 30 minutes and distilled. The distillate was then boiled over phosphorus pentoxide (10 grams per litre) for 30 minutes and distilled twice.

Dry dimethylformamide was obtained by standing dimethylformamide over ground calcium hydride for one week, filtering, and distilling the filtrate at 15 mm.

Dry ethanol was obtained by dissolving sodium in ethanol (7.5 grams per litre), adding ethyl succinate (25 grams per litre) and boiling for two hours. Dry ethanol was then distilled.

Ethanolic hydrogen chloride was prepared by saturating dry ethanol with hydrogen chloride.

Perchloric acid was 70% w/w analar grade. Dimethylthioformamide was prepared by the method of Willstätter and Wirth[120] modified by Pettit and Garson[116]. Heptane-2,4,6-trione was prepared by the method of Morgan and Drew[117]. Potassium selenosulphate was prepared as described by Förster and co-workers[121], and potassium selenotrithionate was prepared by the method described by Foss[122].

2M-Aqueous sodium hydrogen sulphide was prepared by saturating a 2M-aqueous solution of sodium sulphide nonahydrate (analar grade) with hydrogen sulphide.

Hydrogen selenide was generated by dropping 50% aqueous hydrochloric acid onto aluminium selenide under nitrogen.

0.25 M-And 0.5 M-aqueous sodium hydrogen selenide solutions were prepared by saturating a 0.25 M-or 0.5 M-aqueous solution of sodium hydroxide with hydrogen selenide under nitrogen.

Liquid scintillation counting was carried out with a Beckman LS-100 liquid scintillation system operating at an instrument gain setting of 450. All solutions were counted in the carbon-14 channel to a 2σ accuracy of 0.2%. Counting in the external standard ratio channel was performed six times and an average value taken for the external standard ratio.

Volumetric glassware was grade B (E-Mil, gold line) except for 1.0 ml. pipettes and a burette which were grade A (E-Mil, green line).

A scintillation mix was prepared by dissolving Beckman TLA Fluoralloy Dry Mix (8.5 grams) in scintillation grade toluene (1 litre)

giving a concentration of 8 grams per litre 2-(4'-t-butylphenyl)-5-(4"-biphenyl)-1,3,4-oxdiazole (butyl PBD, primary liquid scintillation fluor) and 0.5 grams per litre 2-(4'-biphenyl)-6-phenyl-benzoxazole (PBBO, secondary liquid scintillation fluor).

A standard solution was prepared by dissolving n-hexadecane-1-C14 (10.0 ml., 1.10 μCi/gram) in scintillation mix (100 ml.) giving a solution containing 0.08514 μCi/ml. corresponding to a disintegration rate of 1.89×10^5 disintegrations per minute per ml.. This solution was used as a secondary standard[118] for determining sulphur-35 since the β-spectra of the two isotopes are almost identical.

A sodium sulphide-S35 solution was prepared by dissolving sodium sulphide-S35 (39 mg., initial activity 1.16 m Ci on 22/3/71) with sodium sulphide nonahydrate (200 grams) in water (500 ml.) giving an initial specific activity of sulphur-35 of ca. 1.45 μ Ci/mmole. The sodium sulphide-S35 solution was standardised for sulphide by the method of Bethge[119]. The values of 1.63 M and 1.57 M were found before and after completion of the tracer experiments. The average value, 1.60 M, was taken and used for all calculations.

I Preparation of bis(1,2-diselenolium)tetrachloroferrates (II) (18)

Anhydrous iron(III) chloride (16.3 g., 100 mmoles) and the 1,3-diketone (150 mmoles) were dissolved in ethanolic hydrogen chloride and the solution was cooled to 0^{o}. Hydrogen selenide (600 mmoles, from aluminium selenide 58 g.) was bubbled slowly through the solution under nitrogen, with magnetic stirring. After 4 hours, the mixture was diluted with ether (2 l.), when the bis(1,2-diselenolium)tetrachloroferrate (II) precipitated as dark crystals. The salt was filtered off, washed with benzene to remove neutral material, then washed thoroughly with ether collecting all washings, and finally dried.

(1) Bis(3,5-dimethyl-1,2-diselenolium)tetrachloroferrate (II) (18a).

Acetylacetone (15.0 ml., 150 mmoles) in ethanolic hydrogen chloride (150 ml.), gave bis(3,5-dimethyl-1,2-diselenolium)tetrachloroferrate (II) (18a) (16.5 g., 34%). A sample was recrystallised from ethanolic hydrogen chloride as deep violet prisms, m.p. 95-97^{o} (Found: C, 18.7; H, 2.3. $C_{10}H_{14}Se_4FeCl_4$ requires C, 18.5; H, 2.2%). The combined ether filtrate and all washings were washed well with water, dried and evaporated to dryness. The crystalline residue was chromatographed on a column of alumina (25 x 2.5 cm.) with benzene as eluant. Evaporation of the pale yellow fraction gave a crystalline residue which was recrystallised from cyclohexane giving 1,3,5,7-tetramethyl-2,4,6,8-tetraselenaadamantane (19a) (6.91 g., 20%) as white needles, m.p. 165-166^{o}; M^{+} at $^{m}/_{e}$ 454, (Found: C, 26.9; H, 3.7; $C_{10}H_{16}Se_4$ requires C, 26.6; H, 3.6%).

(2) Bis(3-methyl-5-phenyl-1,2-diselenolium)tetrachloroferrate (II) (18b)

Benzoylacetone (24.33 g., 150 mmoles) in ethanolic hydrogen chloride (375 ml.) gave bis(3-methyl-5-phenyl-1,2-diselenolium) tetrachloroferrate (II) (18b) (26.2 g., 45%). A sample was recrystallised

from ethanolic hydrogen chloride as dark, olive green needles, m.p. 97-99° (Found: C, 31.0; H, 2.3. $C_{20}H_{18}Se_4FeCl_4$ requires C, 31.1; H, 2.4%). The combined ether filtrate and all washings were treated as described in part (1) above and the residual gum chromatographed. Evaporation of the initial fraction (150 ml.) gave a pale yellow gum (2.1 g.) which could not be crystallised although it was shown by T.L.C. to be homogeneous. This material was rejected.

(3) Bis (3-ethyl-4-methyl-1,2-diselenolium) tetrachloroferrate (II) (18c).

2-Hydroxymethylene-pentane-3-one b.p. 60-65°/20 mm., (lit.[110] 75-85°/45-50 mm.), was prepared in 57% yield according to the method used for 2-hydroxymethylene cyclohexanone[111]. 2-Hydroxymethylene-pentane-3-one (17.1 g., 150 mmoles) in ethanolic hydrogen chloride (300 ml.) gave bis (3-ethyl-4-methyl-1,2-diselenolium tetrachloroferrate (II) (18c) (19.47 g., 38%). A sample was recrystallised from ethanolic hydrogen chloride as deep purple needles, m.p. 76-79° (Found: C, 21.5; H, 2.9. $C_{12}H_{18}Se_4FeCl_4$ requires C, 21.3; H, 2.7%). The combined ether filtrate and all washings were washed well with water, dried and evaporated. The gummy residue was chromatographed on a column of alumina (35 x 3.5 cm.) with petrol-benzene (1:1) as eluant. The first fraction (450 ml.) was rejected. Continued elution with benzene gave a fraction (400 ml.) which, after evaporation, gave an oily, semi-crystalline solid which was shown to be impure by T.L.C., The material was rechromatographed on a column of silica (40 x 2.5 cm.) with petrol-benzene (1:1) as eluant. The initial fraction (400 ml.) was rejected and the following fraction (300 ml.) gave, after evaporation, a colourless, crystalline solid (1.474 g., 4.1%) which was recrystallised from cyclohexane giving 1,3-diethyl-9,10-dimethyl-2,4,6,8-tetraselenaadamantane (19c) (1.422 g., 4.0%) as colourless

prisms, m.p. 159-196°, M^+ at $^m/_e$ 482, (Found: C, 30.4; H, 4.5. $C_{12}H_{20}Se_4$ requires C, 30.0; H, 4.2%).

(4) Attempted preparation of bis (3-ethyl-4-methyl-1,2-dithiolium) tetrachloroferrate (II) (23).

(i) When the above reaction, section (I) part (3), was repeated using hydrogen sulphide in place of hydrogen selenide under nitrogen, no bis (1,2-dithiolium) tetrachloroferrate (II) was precipitated on diluting the mixture with ether. Subsequent work up for the tetrathiaadamantane gave, after chromatography on a column of alumina (30 x 3.5 cm.) with benzene as eluant, a colourless gum (18.3 g.). T.L.C. of this material in petrol-benzene (1:1) showed at least five components in good yield and consequently the material was rejected.

(ii) In a second attempt, anhydrous iron(III) chloride (10.9 g., 66.6 mmoles) was dissolved in ethanolic hydrogen chloride (100 ml.) and the solution was cooled to 0°. Hydrogen sulphide was bubbled through this solution with magnetic stirring for one hour. A solution of 2-hydroxymethylene-pentane-3-one (11.4 g., 100 mmoles) in ethanolic hydrogen chloride (100 ml.) was added dropwise, with stirring and continued passage of hydrogen sulphide, over 4 hours. After this period the mixture was diluted with ether (1 l.); there was no precipitate of bis (3-ethyl-4-methyl-1,2-dithiolium) tetrachloroferrate (II).

II Preparation of tris (1,3-diselenato) iron (III) complexes (20).

The same procedure was used here as for the preparation of the bis(1,2-diselenolium) tetrachloroferrates (II) in section (I). The complex, after filtering off, was washed well with water to remove any salt, then washed with ethanol and finally ether before being dried.

(1) Tris(2-selenoformylcyclohexane-1-selenato) iron (III) (20d).

2-Hydroxymethylene cyclohexanone[111] (18.9 g., 150 mmoles) in ethanolic hydrogen chloride (300 ml.) gave tris(2-selenoformylcyclohexane -1-selenato) iron (III) (20d), (17.19 g., 42%). A sample was recrystallised from chloroform (addition of ether) as a brown amorphus powder, decomposing above 100°, (Found: C, 31.2; H, 3.4. $C_{21}H_{27}Se_6Fe$ requires C, 31.2; H, 3.4%). The combined ether filtrate and washings were washed well with water, dried and evaporated. The residual pale brown gum was chromatographed on a column of alumina (60 x 2.5 cm.) with petrol-benzene (1:1) as eluant. The initial pale yellow fraction (200 ml.) was rejected. Three fractions were collected as follows: (1) petrol-benzene (1:1) (150 ml.) shown by T.L.C. to be homogeneous, (2) benzene (200 ml.) shown by T.L.C. to be impure and (3) benzene (350 ml.) shown by T.L.C. to be homogeneous. The impure fraction was evaporated and the residue was rechromatographed giving two pure fractions which were combined with the initial corresponding fractions. Evaporation of fraction (1) followed by rechromatography on a column of alumina (30 x 3.5 cm.) afforded colourless eluates which, on evaporation, gave 2,10,17-triselena-tetracyclo-[7,7,1,0,^{3,8}0,^{11,16}] heptadeca-$\Delta^{3,8}$,$\Delta^{11,16}$-diene (21) (6.12 g., 19%). The diene was recrystallised from cyclohexane as colourless needles, (4.5 g., 14%), m.p. 166-168° (decomposition), M^+ at $^m/_e$ 424, (Found: C, 40.1; H, 4.5. $C_{14}H_{18}Se_3$ requires C, 39.8; H, 4.3%). λ_{max} 209.5 and 243.5 nm. (log ϵ 3.99 and 4.07). The N.M.R. spectrum ($CDCl_3$) showed a broad multiplet (8H) at δ 1.6-2.0 (5,6,13 + 14-CH_2), a broad singlet (8H) at δ 2.1 - 2.5 (4,7,12 + 15-CH_2) and a singlet (2H) at δ 4.65 (1 + 9 - H). Evaporation of fraction (3) followed by rechromatography on a column of alumina (30 x 3.5 cm.) afforded colourless

eluates, which, on evaporation gave bis(1,9; 3,10)-cyclohexano-2,4,6,8-tetraselenaadamantane (19d) (6.53 g., 17%). The tetraselenaadamantane was recrystallised from cyclohexane as colourless needles, (3.06 g., 8.1%), m.p. 164-165°, M^+ at $^m/_e$ 506, (Found: C, 33.7; H, 4.3. $C_{14}H_{20}Se_4$ requires C, 33.4; H, 4.0%).

(2) Tris(3-selenobut-1-ene-1-selenato) iron (III) (20e).

4,4-Dimethoxybutane-2-one (19.8 g., 150 mmoles), in ethanolic hydrogen chloride (300 ml.), gave tris(3-selenobut-1-ene-1-selenato) iron (III) (20e), (31.4 g., 91%). A sample was recrystallised from chloroform (addition of ether) as a green amorphous powder, decomposing above 100°. (Found: C, 20.6; H, 1.9. $C_{12}H_{15}Se_6Fe$ requires C, 20.9; H, 2.2%). The combined ether filtrate and washings were washed well with water, dried and evaporated. The crystalline residue was chromatographed on a column of alumina (30 × 2.5 cm) with benzene as eluant. The pale yellow eluants were evaporated to dryness and the residue rechromatographed. The pale yellow eluants gave, on evaporation, 1,3-dimethyl-2,4,6,8-tetraselenaadamantane (19e) (818 mg., 2.6%) which was recrystallised from benzene as colourless prisms (388 mg., 1.2%), m.p. 273-275°, M^+ at $^m/_e$ 426, (Found: C, 22.9; H, 2.9. $C_8H_{12}Se_4$ requires C, 22.7; H, 2.9%).

III Preparation of 1,2-diselenolium perchlorates (28).

The bis(1,2-diselenolium) tetrachloroferrate (II) (25 mmoles) was suspended in acetic acid (30 ml.) and perchloric acid (25.2 ml., 300 mmoles) was added. The mixture was swirled and heated at 30° until the suspension became pale cream in colour. After allowing the mixture to stand at room temperature for 30 minutes, excess ether was added slowly, when the perchlorate salt precipitated. The salt was filtered off and washed well

with ether. Complete conversion to the perchlorate was ensured by repeating the above treatment with perchloric acid. The 1,2-diselenolium perchlorate, after recrystallisation from 10% v/v perchloric acid-acetic acid (addition of ether), was filtered off, washed well with ether and dried.

(1) 3,5-Dimethyl-1,2-diselenolium perchlorate (28a).

Bis(3,5-dimethyl-1,2-diselenolium) tetrachloroferrate (II) (18a) (16.19 g., 25 mmoles) gave 3,5-dimethyl-1,2-diselenolium perchlorate (28a) (13.17 g., 81%) as cream prisms, m.p. 61-62°, (Found: C, 18.7; H, 2.3. $C_5H_7Se_2ClO_4$ requires C, 18.5; H, 2.2%).

(2) 3-Methyl-5-phenyl-1,2-diselenolium perchlorate (28b).

Bis(3-methyl-5-phenyl-1,2-diselenolium) tetrachloroferrate (II) (18b) (19.3 g., 25 mmoles) gave 3-methyl-5-phenyl-1,2-diselenolium perchlorate (28b) (15.78 g., 82%) as yellow-brown needles, m.p. 109-110°, (Found: C, 31.1; H, 2.3. $C_{10}H_9Se_2ClO_4$ requires C, 31.1; H, 2.4%).

(3) 3-Ethyl-4-methyl-1,2-diselenolium perchlorate (28c).

Bis(3-ethyl-4-methyl-1,2-diselenolium) tetrachloroferrate (II) (18c) (16.9 g., 25 mmoles) gave 3-ethyl-4-methyl-1,2-diselenolium perchlorate (28c) (12.25 g., 72%) as colourless plates, m.p. 99-100°, (Found: C, 21.6; H, 2.9; Se, 46.7. $C_6H_9Se_2ClO_4$ requires C, 21.3; H, 2.7; Se, 46.7%).

IV Preparation of 3-(2-dimethylaminovinyl)-1,2-diselenolium salts (29).

(1) From 3,5-dimethyl-1,2-diselenolium perchlorate.

Dimethylthioformamide (2.1 ml., 25 mmoles) was added to a suspension of 3,5-dimethyl-1,2-diselenolium perchlorate (28a) (3.245 g., 10 mmoles)

in acetic anhydride (40 ml.) and the mixture was boiled for one minute. The solution was allowed to cool, excess ether was added, and the mixture cooled at 0° for 3 hours. The ether layer was decanted and the residual red oil, which could not be crystallised, was washed with ether. This oil was used immediately in further reactions.

(2) From 3-methyl-5-phenyl-1,2-diselenolium perchlorate.

3-Methyl-5-phenyl-1,2-diselenolium perchlorate (28b) (3.365 g., 10 mmoles) was treated as described in part (1) above, boiling the mixture for 5 minutes. After adding the excess ether, the mixture was cooled overnight at 0°, the ether layer was decanted and the residual red oil, which could not be crystallised, was washed with ether. This oil was used immediately in further reactions.

(3) From 3-ethyl-4-methyl-1,2-diselenolium perchlorate.

Dimethylthioformamide (2.1 ml., 25 mmoles) was added to a suspension of 3-ethyl-4-methyl-1,2-diselenolium perchlorate (28c) (6.77 g., 20 mmoles) in acetic anhydride (80 ml.) and the mixture was boiled for 5 minutes. The solution was allowed to cool to room temperature, then cooled in ice-water for 1 hour when deep purple spars precipitated. 3-(2-dimethylamino-1-methylvinyl)-4-methyl-1,2-diselenolium perchlorate (29c) was filtered off, washed well with ether, and recrystallised from acetonitrile (addition of ether) as deep red needles (4.41 g., 56%), m.p. 164-165°. (Found: C, 27.6; H, 3.6; N, 3.6. $C_9H_{14}Se_2NClO_4$ requires C, 27.5; H, 3.6; N, 3.6%). λ_{max} (methanol) 216, 344 and 469 nm. (log ε 3.88, 3.81 and 2.91). The N.M.R. spectrum (d_6-DMSO) showed a singlet (3H) at δ 2.10 (CH_3-C=C), a singlet (3H) at δ 2.44 (4-CH_3), a singlet (6H) at δ 3.38 [$N(CH_3)_2$], a singlet (1H) at δ 8.48 (C=CH) and a singlet (1H) at δ 8.62

(5-H). In TFA-perchloric acid solution, the N.M.R. spectrum showed a doublet (3H) at δ 2.18 ($J_{CH_3,H}$ = 6.5 Hz) (CH_3-CH), a singlet (3H) at δ 2.88 (4-CH_3), a singlet (6H) at δ 3.98 [$N(CH_3)_2$], a very broad peak (1H) centred at δ 5.1 (CH_3-CH), a broad peak (1H) at δ 8.7-8.9 [$CH=\overset{+}{N}(CH_3)_2$], and a singlet (1H) at δ 11.51 (5-H).

On a large scale, 3-ethyl-4-methyl-1,2-diselenolium perchlorate (28c) (16.93 g., 50 mmoles) with dimethylthioformamide (5.3 ml., 62.5 mmoles) in acetic anhydride (200 ml.) gave 3-(2-dimethylamino-1-methylvinyl)-4-methyl-1,2-diselenolium perchlorate (29c) (8.66 g., 44%). The combined filtrate and ether washings were diluted with water and extracted with benzene. The washed, dried extracts were evaporated and the red, crystalline residue chromatographed on a column of alumina (30 x 2.5 cm.) with benzene as eluant. Evaporation of the initial red eluates gave a crystalline residue which was rechromatographed. The red eluants, on evaporation, afforded 3,4-dimethyl-1,6-dithia-6a-selenapentalene (32c) (521 mg., 4.4%), which was recrystallised from cyclohexane as red needles (383 mg., 3.3%), m.p. 139-141°, (Found: C, 36.0; H, 3.6; Se, 34.2. $C_7H_8S_2Se$ requires C, 35.8; H, 3.4; Se, 33.6%). Continued elution with benzene-ether (4:1) afforded yellow eluates which were evaporated and the residue was rechromatographed. Evaporation of the yellow eluates afforded 3-(1-acetylethylidene)-4-methyl-3H-1,2-diselenole (31) (314 mg., 2.2%) which was recrystallised from petrol as yellow needles (180 mg., 1.3%), m.p. 94-95°, (Found: C, 34.7; H, 3.7. $C_8H_{10}Se_2O$ requires C, 34.3; H, 3.6%).

(4) <u>From tris(2-selenoformylcyclohexane-1-selenato) iron (III).</u>

Tris(2-selenoformylcyclohexane-1-selenato) iron (III) (20d)

(4.045 g., 5 mmoles) was heated with a mixture of phosphoryl chloride (2.8 ml., 30 mmoles) and dimethylformamide (20 ml.) up to 100° over 15 minutes. After 15 minutes at 100°, the deep red solution was allowed to cool. This solution was used immediately in further reactions.

(5) From tris(3-selenobut-1-ene-1-selenato) iron (III).

Phosphoryl chloride (2.3 ml., 25 mmoles) was added to a suspension of tris(3-selenobut-1-ene-1-selenato) iron (III) (20e) (3.1 g., 4.5 mmoles) in dimethylthioformamide (20 ml.) and the mixture was heated to 100° over 15 minutes. Excess ether was added to the cooled solution and the mixture was cooled at 0° for 30 minutes. After decanting the ether, the residual oil was washed with ether, dissolved in dimethylformamide (20 ml.) and excess ether was added. The mixture was cooled for 30 minutes at 0°, the ether was decanted and the residual oil washed with ether. This procedure was repeated once more to remove dimethylthioformamide . The resulting red oil was used immediately in further reactions.

V Preparation of 3-acylmethylene-3H-1,2-diselenoles (35).

(1) 3-Formylmethylene-5-methyl-3H-1,2-diselenole (35a).

2 M-Aqueous sodium hydroxide (50 ml., 100 mmoles) was added to a solution of the oil, prepared as described in section (IV) part (1), in dimethylformamide (50 ml.). The mixture was swirled for 1 minute, diluted with water, and extracted with ether. Evaporation of the washed, dried extracts gave a yellow residue which was chromatographed on a column of alumina (30 x 2.0 cm.) with benzene as eluant. Elution with benzene-ether (5:1) gave yellow eluates which, on evaporation, afforded 3-formylmethylene-5-methyl-3H-1,2-diselenole (35a) (302 mg., 12%). Recrystallisation of the residue from cyclohexane gave yellow prisms (138 mg., 5.5%), m.p. 111-112° (Found: C, 28.9; H, 2.5. $C_6H_6Se_2O$

requires C, 28.6; H, 2.4%).

(2) 3-Formylmethylene-5-phenyl-3H-1,2-diselenole (35b).

2 M-Aqueous sodium hydroxide (25 ml., 50 mmoles) was added to a solution of the oil, prepared as described in section (IV) part (2), in acetonitrile (100 ml.). The mixture was swirled for 1 minute, diluted with water, and extracted with benzene. Evaporation of the washed, dried extracts gave a yellow oil which was chromatographed on a column of alumina (50 x 2.5 cm.) with benzene initially as eluant. Elution with benzene-ether (6:1) gave a yellow-brown fraction which was evaporated and the residue rechromatographed. The yellow-brown eluates, after evaporation, gave a crystalline solid which was boiled with activated charcoal in acetonitrile. Evaporation of the yellow filtrate gave 3-formylmethylene-5-phenyl-3H-1,2-diselenole (35b) (224 mg., 7.1%), which recrystallised from cyclohexane as deep yellow prisms, m.p. 89-90°, (Found: C, 42.4; H, 2.7. $C_{11}H_8Se_2O$ requires C, 42.1; H, 2.6%). Continued elution with benzene-ether (5:1) gave a further yellow-brown fraction which was evaporated and the residue rechromatographed. The yellow-brown eluates, after evaporation, afforded a yellow-brown residue which was boiled with activated charcoal in acetonitrile. Evaporation of the yellow filtrate gave a crystalline residue (114 mg., 3.2%) which, on recrystallisation from cyclohexane, afforded 3-(1-formyl-1-acetylmethylene)-5-phenyl-3H-1,2-diselenole (35f) as yellow needles, m.p. 120-125° and 133-135°, M^+ at $^m/_e$ 358 (100%), (Found: C, 43.7; H, 2.8. $C_{13}H_{10}Se_2O_2$ requires C, 43.8; H, 2.8%).

(3) 3-(1-Formylethylidene)-4-methyl-3H-1,2-diselenole (35c).

2 M-Aqueous sodium hydroxide (25 ml., 50 mmoles) was added to a

solution of 3-(2-dimethylamino-1-methylvinyl)-4-methyl-1,2-diselenolium perchlorate (29c) (1.968 g., 5 mmoles) in acetonitrile (100 ml.) at 0°. After 5 minutes the mixture was diluted with water and extracted with benzene. The washed, dried extracts were evaporated and the crystalline residue was chromatographed on a column of alumina (30 x 2.5 cm.) with benzene as eluant. An initial yellow-green fraction was evaporated and the residue rechromatographed. Evaporation of the green eluates afforded 3,5-dimethyl-4H-1-pyran-4-selenoketone (36a) (134 mg., 14%) which was recrystallised from cyclohexane as red-brown needles, m.p. 159° (sublimation above 130°), M^+ at $^m/_e$ 188 (100%), (Found: C, 45.0; H, 4.5. C_7H_8SeO requires C, 44.9; H, 4.3%). Continued elution with benzene-ether (3:1) afforded yellow eluates which, on evaporation, gave 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole (35c) (773 mg., 58%), recrystallised from cyclohexane as yellow spars (692 mg., 52%), m.p. 131-132°, (Found: C, 31.7; H, 3.1. $C_7H_8Se_2O$ requires C, 31.6; H, 3.0%).

Treatment of 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole (35c) with aqueous sodium hydroxide.

The acylmethylene-3H-1,2-diselenole (35c) (1.33 g., 5 mmoles) was dissolved in acetonitrile (100 ml.) and treated with 2M-aqueous sodium hydroxide (25 ml., 50 mmoles) under the same conditions as described in part (3) above. Subsequent work up afforded recovered starting material in 99% yield.

(4) 3-Formyl-5,6-dihydro-4H-benzo[C][1,2] diselenole (35d).

(i) Dimethylformamide (30 ml.) and ethanol (50 ml.) were added to the solution prepared as described in section (IV) part (4) followed by

2M-aqueous sodium hydroxide (30 ml., 60 mmoles). The mixture was swirled for 1 minute, diluted with water, and extracted with benzene. The filtered extracts were washed well with water, dried and evaporated. The residual oil was chromatographed on a column of alumina (30 x 2.5 cm.) with benzene as eluant. Evaporation of the initial blue eluates gave a residue which was rechromatographed. The blue eluates, on evaporation, afforded 4,5-dihydro-3H-benzo[cd]1,6,6a-triselenapentalene (41d) as a deep blue oil (214 mg., 4.2%) which slowly crystallised. The triselenapentalene was recrystallised from methanol as deep purple needles (181 mg., 3.5%) identical (by N.M.R.) with a sample prepared using aqueous sodium hydrogen selenide [section (VII) part (4i)]. Continued elution with ether gave a yellow-brown fraction which was evaporated and the residue rechromatographed on a column of silica (30 x 2.0 cm.) with benzene-ether (4:1) as eluant. The yellow-brown eluates, after evaporation, gave a crystalline solid which was boiled with activated charcoal in ethanol. Evaporation of the yellow filtrates afforded a residue (273 mg., 6.5%) which, after recrystallisation from petrol, gave 3-formyl-5,6-dihydro-4H-benzo[c][1,2]diselenole (35d) as yellow plates (156 mg., 3.7%), m.p. 91-93°, (Found: C, 34.8; H, 2.9. $C_8H_8Se_2O$ requires C, 34.6; H, 2.9%).

(ii) In a second run, tris(2-selenoformylcyclohexane -1-selenato) iron (III) (20d) (3.5 g., 4.3 mmoles), phosphoryl chloride (2.3 ml., 25 mmoles) and dimethylthioformamide (20 ml.) were treated as described in section (IV) part (4). Excess ether was added to the deep red solution and the mixture allowed to stand at 0° for 1 hour. The ether layer was decanted from the red oil (see below), washed with water, dried,

evaporated and the residue chromatographed on a column of alumina (30 x 2.0 cm.) with benzene as eluant. The red eluates, on evaporation, gave a residue which was rechromatographed. Evaporation of the red eluates gave a crystalline residue (48 mg.) of 4,5-dihydro-3H-benzo[cd]1,6-dithia-6a-selenapentalene (32d) [section (VIII) part (2)] which was 90% pure. The N.M.R. spectrum ($CDCl_3$) showed a 10% impurity of 4,5-dihydro-3H-benzo [cd]-1-thia-6,6a-diselenapentalene (42d) [section (VI) part (5)]. After decanting the ether layer, the residual red oil was dissolved in dimethylformamide-ethanol (1:1) (100 ml.) and 2M-aqueous sodium hydroxide (25 ml.,50 mmoles) was added. Work up as described in part (4i) above gave a purple oil (92 mg.) and 3-formyl-5,6-dihydro-4H-benzo[c][1,2] diselenole (35d) (130 mg., 3.6%) which was recrystallised from petrol as yellow plates (88 mg., 2.4%). The N.M.R. spectrum of the purple oil ($CDCl_3$) showed it to be a mixture of 4,5-dihydro-3H-benzo[cd] 1,6-dithia-6a-selenapentalene (32d), 4,5-dihydro-3H-benzo[cd] 1-thia-6,6a-diselenapentalene (42d), and 4,5-dihydro-3H-benzo[cd] 1,6,6a-triselenapentalene (41d) in the ratio (by integral) 1:4:1.

(5) Attempted Preparation of 3-formylmethylene-3H-1,2-diselenole (35e).

2M-Aqueous sodium hydroxide (25 ml., 50 mmoles) was added to a filtered solution of the oil, prepared as described in section (IV) part (5), in acetonitrile (240 ml.). The mixture was swirled, diluted with water, and extracted with benzene. The washed, dried extracts gave, on evaporation, an orange oil which was chromatographed on a column of alumina (30 x 2.0 cm.) with benzene as eluant. The initial red eluates were evaporated and the residue was rechromatographed. Evaporation of the red eluates gave a crystalline solid (45 mg.) which was shown by N.M.R. ($CDCl_3$) to be a mixture of 1,6-dithia-6a-selenapentalene (32e),

characterised by Reid [99], and 1-thia-6,6a-diselenapentalene (42e) in the ratio 1:2. Continued elution with benzene-ether (6:1) gave yellow eluates which were evaporated. The residual yellow oil was rechromatographed on a column of silica (60 x 1.5 cm.) with benzene-ether (6:1) as eluant. The yellow eluates, on evaporation, afforded a yellow oil (80 mg.) which did not crystallise. The N.M.R. spectrum ($CDCl_3$) showed the oil to consist of impure 3-formylmethylene-3H-1,2-diselenole (35e). The impurity (ca. 10%) could not be removed by chromatography. The mass spectrum showed peaks at $^{m}/_{e}$ 240, $C_5H_4Se_2O$ 3-formylmethylene-3H-1,2-diselenole (35e) and $^{m}/_{e}$ 192, probably C_5H_4SeSO 3-formylmethylene-3H-1,2-thiaselenole (43).

VI Preparation of 1-thia-6,6a-diselenapentalenes (42).

(1) 5-Methyl-1-thia-6,6a-diselenapentalene (42a).

2M-Aqueous sodium hydrogen sulphide (50 ml., 100 mmoles) was added to a solution of the oil, prepared as described in section (IV) part (1), in dimethylformamide-ethanol (1:1) (100 ml.). The mixture was swirled for 1 minute, diluted with water, and extracted with ether. Evaporation of the washed, dried extracts gave a deep purple residue which was chromatographed on a column of alumina (50 x 2.0 cm.) with benzene as eluant. The deep red eluates, on evaporation, afforded 5-methyl-1-thia-6,6a-diselenapentalene (42a) (427 mg., 16%) which recrystallised from cyclohexane as red plates (284 mg., 11%), m.p. 148°, (Found: C, 27.1; H, 2.3. $C_6H_6Se_2S$ requires C, 26.9; H, 2.3%).

(2) 2,5-Dimethyl-1-thia-6,6a-diselenapentalene (42g).

N,N-Dimethylthioacetamide (5.15 g., 50 mmoles) was added to a suspension of 3,5-dimethyl-1,2-diselenolium perchlorate (28a) (3.245 g.,

10 mmoles) in acetic anhydride (40 ml.) and the mixture treated as described in section (IV) part (1). The resulting oil, in dimethylformamide-ethanol (1:1) (100 ml.), was reacted with 2M-aqueous sodium hydrogen sulphide as described in part (1) above. Subsequent work up and chromatography of the residue on a column of alumina (50 x 2.0 cm.) with benzene-petrol (2:1) as eluant gave initial red eluants which were evaporated. The residue (49 mg., 1.7%) was recrystallised from cyclohexane giving 2,5-dimethyl-1-thia-6,6a-diselenapentalene (42g) as red needles, sublimed above 175° (decomposition) (lit.[100] m.p. 215-216°), identical, by I.R. in carbon disulphide and carbon tetrachloride, with spectra recorded by Mammi.[55] (Found: C, 29.9; H, 2.8. $C_7H_8Se_2S$ requires C, 29.8; H, 2.9%). Continued elution with benzene-ether (5:1) gave red eluates which were evaporated and the residue rechromatographed. The initial red eluates were rejected. Further elution with benzene-ether (5:1) gave orange eluates which, on evaporation, afforded a brown crystalline residue (52 mg., 3.4%). The residue was recrystallised from cyclohexane giving a compound (44) of unknown structure as brown prisms, m.p. 143-144°, M^+ at $^m/_e$ 300 (100%) (high resolution 299.946, calculated for $C_{12}H_{12}SeS_2$ is 299.955), (Found: C, 48.2; H, 4.1. $C_{12}H_{12}SeS_2$ requires C, 48.2; H, 4.0%). λ_{max} 205, 244, 326, 334(s), 356, 373 and 465 nm., (log ϵ 4.09, 4.08, 4.21, 4.17, 4.10, 4.10 and 3.78). The mass spectrum showed intense peaks at $^m/_e$ 300, 285, 256, 241, 220 and 149, all containing selenium except the peak at 220. The N.M.R. spectrum ($CDCl_3$) showed a singlet (3H) at δ 2.27 (CH_3), a doublet (3H) at δ 2.38 (J = 0.8 Hz) (CH_3), a doublet (3H) at δ 2.55 (J = 0.8Hz) (CH_3), a broad singlet (1H) at δ 6.84, a broad singlet (1H) at δ 7.00 and a singlet (1H) at δ 7.49. The I.R. spectrum (nujol mull) showed medium to strong absorption at 1590, 1500,

1322, 1256, 1231, 1050, 1010, 908, 868 and 818 cm^{-1}.

(3) 5-Phenyl-1-thia-6,6a-diselenapentalene (42b).

2M-Aqueous sodium hydrogen sulphide (50 ml., 100 mmoles) was added to a solution of the oil, prepared as described in section (IV) part (2), in dimethylformamide-ethanol (1:1) (100 ml.). The mixture was swirled for 1 minute, diluted with water, and extracted with ether. Evaporation of the washed, dried extracts gave a residue which was chromatographed on a column of alumina (60 x 1.5 cm.) with benzene-petrol (1:1) as eluant. The initial dark red eluates, on evaporation, yielded a crystalline solid (287 mg., 8.7%) which, after recrystallisation from cyclohexane, afforded 5-phenyl-1-thia-6,6a-diselenapentalene (42b) (194 mg., 6.0%) as deep purple needles, m.p. 120°, (Found: C, 39.9; H, 2.5. $C_{11}H_8Se_2S$ requires C, 40.0; H, 2.4%). Further elution with benzene-ether (1:1) afforded purple eluates which were shown by T.L.C. to be impure. The residue, after evaporation, was rechromatographed on a column of silica (55 x 1.5 cm.) with benzene as eluant. An initial purple fraction was rejected. Evaporation of the red eluates gave a crystalline solid (114 mg., 3.1%) which, after recrystallisation from cyclohexane, afforded 3-acetyl-5-phenyl-1-thia-6,6a-diselenapentalene (42f) (50 mg., 1.3%) as red needles, m.p. 176-177°, M^+ at $^m/_e$ 374, (Found: C, 42.1; H, 2.8. $C_{13}H_{10}Se_2SO$ requires C, 42.0; H, 2.7%).

(4) Attempted preparation of 3,4-dimethyl-1-thia-6,6a-diselenapentalene (42c)

(i) From the Vilsmeier salt (29c).

2M-Aqueous sodium hydrogen sulphide (12.5 ml., 25 mmoles) was added to a solution of 3-(2-dimethylamino-1-methylvinyl)-4-methyl-1,2-diselenolium perchlorate (29c) (1.968 g., 5 mmoles) in acetonitrile (100 ml.) at 0°.

The mixture was allowed to stand for 3 minutes, diluted with water and extracted with benzene. The washed, dried extracts, on evaporation, gave a crystalline residue which was chromatographed on a column of alumina (45 x 2.5 cm.) with benzene as eluant. The initial purple eluates were evaporated and the residue rechromatographed. Evaporation of the purple eluates gave a crystalline solid (908 mg.) which recrystallised from cyclohexane as deep purple spars (826 mg.). The N.M.R. spectrum ($CDCl_3$) showed the crystalline material to be a mixture of 3,4-dimethyl-1-thia-6,6a-diselenapentalene (42c) and 3,4-dimethyl-1,6-dithia-6a-selenapentalene (32c) [section (VIII) part (1)] in the ratio 1:1. The mass spectrum showed peaks at $^{m}/_{e}$ 284, compound (42c), and $^{m}/_{e}$ 236, compound (32c). Further elution with benzene, gave a green fraction which was evaporated and the residue rechromatographed. The green eluates, on evaporation, gave 3,5-dimethyl-4H-1-thiopyran-4-selenoketone (36b) (90 mg., 8.9%) as a brown, crystalline solid identical (by N.M.R.) with a sample characterised by Reid.[99] Continued elution with benzene-ether (2:1) gave yellow eluates which, on evaporation, afforded 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole (35c) (48 mg., 3.6%) identical (by N.M.R.) with a sample prepared as described in section (V) part (3).

(ii) From the acylmethylene-3H-1,2-diselenole (35c)

Phosphoryl chloride (0.55 ml., 6 mmoles) was added to a solution of 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole (35c) (1.33 g., 5 mmoles) in dry dimethylformamide (25 ml.). After 5 minutes, a layer of benzene was added immediately followed by a solution of sodium thiosulphate (2.37 g., 15 mmoles) in water (7.5 ml.). The mixture was swirled, diluted with water and extracted with benzene. The washed, dried extracts

were evaporated and the residue chromatographed on a column of alumina (40 x 2.5 cm.) with benzene as eluant. Evaporation of the initial purple eluates and subsequent rechromatography of the residue gave a crystalline solid (583 mg.) which recrystallised from cyclohexane as deep purple spars (511 mg.). The N.M.R. spectrum ($CDCl_3$) showed the crystalline solid to be a mixture of 3,4-dimethyl-1,6-dithia-6a-selenapentalene (32c), 3,4-dimethyl-1-thia-6,6a-diselenapentalene (42c) and 3,4-dimethyl-1,6,6a-triselenapentalene (41c) in the ratio 3:1.5:1 respectively. The mass spectrum showed peaks at $^{m}/e$ 236, 284 and 330 corresponding to the three analogues respectively. Continued elution with benzene-ether (1:1) afforded yellow eluates which, on evaporation, gave recovered starting material (55 mg., 4.1%).

(5) 4,5-Dihydro-3H-benzo[cd]-1-thia-6,6a-diselenapentalene (42d).

Tris (2-selenoformylcyclohexane-1-selenato) iron (III) (20d) (3.4 g., 4.3 mmoles), phosphoryl chloride (2.3 ml., 25 mmoles) and dimethylformamide (20 ml.) were treated as described in section (IV) part (4). Dimethylformamide (30 ml.) and ethanol (50 ml.) were added to the resulting solution and then cooled to 0^{o}. 2M-Aqueous sodium hydrogen sulphide (25 ml., 50 mmoles), cooled to 0^{o}, was added to this solution. The mixture was swirled, diluted with water and extracted with benzene. The filtered extracts were washed, dried and evaporated. Chromatography of the purple residue on a column of alumina (30 x 2.5 cm.) with benzene as eluant gave initial purple eluates which were evaporated. Rechromatography of the residue afforded a purple crystalline solid (310 mg., 8.1%) which, after recrystallisation from methanol, gave 4,5-dihydro-3H-benzo[cd]-1-thia-6,6a-diselenapentalene (42d) as deep

red needles (228 mg., 6.0%), m.p. 92-94°, (Found: C, 32.7; H, 2.8. $C_8H_8Se_2S$ requires C, 32.7; H, 2.7%). Continued elution with benzene-ether (4:1) gave a yellow fraction which was evaporated. Rechromatography of the residue gave 3-formyl-5,6-dihydro-4H-benzo [c] [1,2] diselenole (35d) (84mg., 2.3%) identical (by m.p.) with a sample prepared as described in section (V) part (4).

In an initial experiment, aqueous sodium hydrogen sulphide was added to the solution at room temperature. Work up as described above afforded a purple residue (411 mg.) which recrystallised from methanol as deep red feathers (283 mg.). The N.M.R. spectrum ($CDCl_3$) showed the presence of 4,5-dihydro-3H-benzo[cd]-1,6-dithia-6a-selenapentalene (32d) as an impurity (ca. 15%). Further recrystallisation made no significant change in the composition of the product.

(6) Attempted preparation of 1-thia-6,6a-diselenapentalene (42e).

The tar, prepared as described in section (IV) part (5), was extracted with hot acetonitrile (6 x 40 ml.) and the solution was filtered. After evaporation to ca. 20 ml., excess ether was added and the mixture cooled at 0° for 1 hour. The ether layer was decanted and the residual oil washed with ether. 2M-Aqueous sodium hydrogen sulphide (25 ml., 50 mmoles) was added to a solution of the oil in acetonitrile (200 ml.). The mixture was swirled, diluted with water, and extracted with benzene. The washed, dried extracts, on evaporation, gave a red residue which was chromatographed on a column of alumina (30 x 2.0 cm.) with benzene as eluant. Evaporation of the red eluates and rechromatography of the residue afforded a red crystalline solid (57 mg.). The N.M.R. spectrum ($CDCl_3$) showed this material to be a 1:1 mixture of 1-thia-6,6a-diselenapentalene (42e) and 1,6-dithia-6a-selenapentalene[99] (32e).

VII Preparation of 1,6,6a-triselenapentalenes (41).

(1) 2-Methyl-1,6,6a-triselenapentalene (41a).

Dimethylthioformamide (1.1 ml., 12.5 mmoles), 3,5-dimethyl-1,2-diselenolium perchlorate (1.62 g., 5 mmoles) and acetic anhydride (20 ml.) were treated as described in section (IV) part (1). The resulting oil, in acetonitrile (25 ml.), was filtered and excess ether added to the filtrate. The mixture was cooled at 0° for three hours, the ether decanted and the residual oil washed with ether. 0.25 M-Aqueous sodium hydrogen selenide (50 ml., 12.5 mmoles) was added to a solution of the oil, in acetonitrile (100 ml.) at 0°, under nitrogen. The mixture was swirled for 1 minute, diluted with water and extracted with benzene. Evaporation of the washed, dried extracts gave a purple residue which was chromatographed on a column of alumina (50 x 2.5 cm.) with benzene as eluant. The initial purple eluates were evaporated and the residue rechromatographed. Evaporation of the purple eluates gave a crystalline solid (191 mg., 12%) which, after recrystallisation from cyclohexane, afforded 2-methyl-1,6,6a-triselenapentalene (41a) (138 mg., 8.8%) as reddish-brown plates, m.p. 176-177°, (Found: C, 23.3; H, 2.1 $C_6H_6Se_3$ requires C, 22.9; H, 1.9%).

(2) 2-Phenyl-1,6,6a-triselenapentalene (41b).

The oil, prepared as described in section (IV) part (2) was dissolved in acetonitrile (100 ml.) and excess ether was added. The ether was decanted after cooling the mixture at 0° for 3 hours, and the residual oil was washed with ether. 0.5 M-Aqueous sodium hydrogen selenide (50 ml., 25 mmoles) was added to a solution of the oil, in acetonitrile (200 ml.), at 0° under nitrogen. The mixture was swirled, diluted with water, and extracted with benzene. Evaporation of the

washed, dried extracts gave a residue which was chromatographed on a column of alumina (60 x 2.5 cm.) with benzene as eluant. The initial purple eluates were evaporated and the residue rechromatographed. Evaporation of the purple eluates gave a crystalline solid (359 mg., 10%) which, after recrystallisation from cyclohexane, afforded 2-phenyl-1,6,6a-triselenapentalene (41b) as brown prisms, m.p. 137-138°, (Found: C, 35.1; H, 2.2. $C_{11}H_8Se_3$ requires C, 35.0; H, 2.1%). Continued elution with benzene gave a second purple fraction which was evaporated and the residue rechromatographed. Evaporation of the purple eluates gave a crystalline residue (105 mg., 2.5%) which, after recrystallisation from acetonitrile, afforded 2-phenyl-4-acetyl-1,6,6a-triselenapentalene (41f) as red-brown needles, m.p. 177-178°, M^+ at $^m/_e$ 420. A satisfactory analysis of this compound could not be obtained.

(3) 3,4-Dimethyl-1,6,6a-triselenapentalene (41c).

(i) From the Vilsmeier salt (29c).

(a) 0.25 M-Aqueous sodium hydrogen selenide (50 ml., 12.5 mmoles) was added to a solution of 3-(2-dimethylamino-1-methylvinyl)-4-methyl-1,2-diselenolium perchlorate (29c) (1.968 g., 5 mmoles) in acetonitrile (100 ml.) under nitrogen at 0°. The mixture was swirled for 2 minutes, diluted with water, and extracted with benzene. The washed, dried extracts were evaporated and the crystalline residue chromatographed on a column of alumina (50 x 2.5 cm.) with benzene as eluant initially. 5 Fractions were collected as follows:

(1) An initial blue fraction (100 ml.) was evaporated and the residue, after rechromatography, afforded 3,4-dimethyl-1,6,6a-triselenapentalene (41c) (48 mg., 3.0%) identical (by N.M.R.) with a sample prepared as described in part (iia) below.

(2) A colourless fraction (100 ml.) was evaporated and the residue, after rechromatography, afforded a pale yellow crystalline solid (40 mg., 3.9%) which was recrystallised from petrol giving a compound formulated as 3,4-dimethyl-1,6-dioxa-6a-selenapentalene (48) as pale yellow prisms, m.p. 103-103.5°, M^+ at $^m/_e$ 204 (100%) (high resolution 203.969, calculated for $C_7H_8SeO_2$ is 203.968). (Found: C, 41.2; H, 4.1. $C_7H_8SeO_2$ requires C, 41.4; H, 4.0%). λ_{max} 214, 239.5, 298 and 381 nm (log ϵ 3.70, 3.35, 3.49 and 4.17). The N.M.R. spectrum ($CDCl_3$) showed a singlet (6H) at δ 2.47 (3 + 4 - CH_3) and a singlet (2H) at δ 8.62 (2 + 5 - H). The I.R. spectrum (carbon disulphide) showed medium to strong absorptions at 2970, 1395, 1380, 1280, 1220, 997, 921, 726, and 663 cm^{-1}. In chloroform, a peak at 1456 cm^{-1} was present and as a nujol mull further peaks at 1544 and 1526 cm^{-1} were apparent.

(3) A green fraction (350 ml.) was evaporated and the residue, after rechromatography, afforded a brown crystalline solid (588 mg., 47%) formulated as 3,5-dimethyl-4H-1-selenopyran-4-selenoketone (36c) on the basis of the N.M.R. spectrum (see appendix A, table 7), the mass spectrum which showed M^+ at $^m/_e$ 252 (100%) and its reactivity (see below).

(4) Continued elution with benzene-ether (1:1) afforded a yellow fraction (300 ml.) which was evaporated and the residue, after rechromatography, gave 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole (35c) (125 mg., 9.4%).

(5) Elution with ether gave a colourless fraction (200 ml.) which was evaporated and the residue, after rechromatography, afforded 3,5-dimethyl-4H-1-selenopyran-4-one (49) (68 mg., 7.3%). The brown crystalline solid, 3,5-dimethyl-4H-1-selenopyran-4-selenoketone (36c) from fraction (3) was left dry overnight, then chromatographed on a column of alumina (30 x 2.5 cm.) as described above, with benzene initially as eluant.

Evaporation of the 3 fractions afforded 3,4-dimethyl-1,6-dioxa-6a-selenapentalene (48) (15 mg., 1%), 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole (35c) (160 mg., 12%) and 3,5-dimethyl-4H-1-selenopyran-4-one (49) (212 mg., 23%). The 3-acylmethylene-3H-1,2-diselenole was combined with that obtained previously and the total (285 mg., 21%) was recrystallised from cyclohexane as yellow spars (245 mg., 18%), identical (by m.p.) with a sample prepared as described in section (V) part (3). The selenopyran-4-one was combined with that obtained previously and the total (280 mg., 30%), after recrystallisation from petrol, afforded 3,5-dimethyl-4H-1-selenopyran-4-one (49) (188 mg., 20%) as colourless needles, m.p. 50-50.5°, M^+ at $^m/_e$ 188 (100%), (Found: C, 45.2; H, 4.6. C_7H_8SeO requires C, 44.9; H, 4.3%).

(b) In a second experiment, the products were extracted with chloroform and the washed, dark green solution left overnight. The original dark green solution turned yellow and selenium metal was deposited. This process was found to be greatly accelerated by strong sunlight. The dried, chloroform extract was evaporated and the residue chromatographed on a column of alumina (50 x 2.5 cm.) with benzene initially as eluant. 4 Fractions were collected and worked up as described above. The following products were obtained; 3,4-dimethyl-1,6,6a-triselenapentalene (41c) (18 mg., 1.1%), 3,4-dimethyl-1,6-dioxa-6a-selenapentalene (48) (11 mg., 1.1%), 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole (35c) (135 mg., 10%) and 3,5-dimethyl-4H-selenopyran-4-one (49) (716 mg., 77%) which was recrystallised from petrol as colourless needles (600 mg., 64%).

(ii) <u>From the acylmethylene-3H-1,2-diselenole (35c).</u>

(a) 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole (35c) (1,33 g., 5 mmoles) was treated as described in section (VI) part (4ii) and a

solution of potassium selenosulphate (3.57 g., 15 mmoles) in water (7.5 ml.) at 60° was added. Work up and subsequent chromatography as described in section (VI) part (4ii) gave initial deep blue eluates which were evaporated and the residue rechromatographed. Recrystallisation of the black crystalline solid (566 mg., 34%) from cyclohexane afforded 3,4-dimethyl-1,6,6a-triselenapentalene (41c) (478 mg., 29%) as shiny black plates, m.p. 144-146°, M^+ at $^m/_e$ 330 (100%), (Found: C, 25.5; H, 2.4; Se, 71.7. $C_7H_8Se_3$ requires C, 25.6; H, 2.5; Se, 72.0%). Continued elution with benzene-ether (3:1) gave yellow eluates which, on evaporation, afforded recovered starting material (57 mg., 4.3%).

(b) In a second experiment, oxalyl chloride (0.52 ml., 6 mmoles) and chloroform (25 ml.) were used in place of phosphoryl chloride and dry dimethylformamide. Work up as described in (a) above gave 3,4-dimethyl-1,6,6a-triselenapentalene (39 mg., 2.4%) (41c) and recovered 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole (35c) (561 mg., 42%).

(c) In a third experiment, a solution of potassium selenotrithionate (4.76 g., 15 mmoles) in water (7.5 ml.) at 70° was used in place of the solution of potassium selenosulphate. Work up as described in (a) above gave 3,4-dimethyl-1,6,6a-triselenapentalene (41c) (302 mg., 18%) which recrystallised from cyclohexane as shiny black plates (243 mg., 15%) and recovered 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole (35c) (128 mg., 10%).

(4) 4,5-Dihydro-3H-benzo[cd]-1,6,6a-triselenapentalene (41d).

(i) Via the Vilsmeier salt (29d).

Dimethylformamide (30 ml.) and ethanol (50 ml.) were added to the solution prepared as described in section (IV) part (4) followed by

0.5 M-aqueous sodium hydrogen selenide (75 ml., 37.5 mmoles) under nitrogen. The mixture was swirled, diluted with water, and extracted with benzene. The filtered extracts were washed, dried, and evaporated to give a black oil which was chromatographed on a column of alumina (30 x 2.5 cm.) with benzene-petrol (1:1) as eluant. The initial blue eluates were evaporated and the residue, after rechromatography, gave a deep blue oil (344 mg., 6.7%) which slowly crystallised. The residue, after recrystallisation from methanol, afforded 4,5-dihydro-3H-benzo[cd]-1,6,6a-triselenapentalene (41d) (296 mg.,5.8%) as purple needles, m.p. 98-100°, M^+ at $^m/_e$ 342, (Found: C, 28.2; H, 2.5; Se, 69.2 (average of 2 determinations). $C_8H_8Se_3$ requires C, 28.2; H, 2.4; Se, 69.5%). Continued elution with benzene-ether (4:1) afforded yellow eluates which were evaporated and the residue rechromatographed on a column of silica (30 x 2.0 cm.) with benzene-ether (4:1) as eluant. Evaporation of the yellow eluates gave a crystalline residue (120 mg., 2.9%) which, after recrystallisation from petrol, afforded 3-formyl-5,6-dihydro-4H-benzo[c][1,2] diselenole (35d) as yellow plates (69 mg., 1.7%) identical (by N.M.R.) with a sample prepared as described in section (V) part (4,i).

(ii) From the acylmethylene-3H-1,2-diselenole (35d).

(a) 3-Formyl-5,6-dihydro-4H-benzo[c][1,2] diselenole (35d) (1.39 g., 5 mmoles) was treated as described in section (VII) part (3, ii, a). Work up and subsequent chromatography gave a crystalline residue (898 mg., 53%) which, after recrystallisation from methanol, afforded 4,5-dihydro-3H-benzo[cd]-1,6,6a-triselenapentalene (41d) as deep purple needles (844 mg., 50%) identical (by m.p.) with a sample prepared as described in part (i) above. Elution with benzene-ether (4:1) afforded yellow

eluates which contained recovered starting material (31 mg., 2.2%).

(b) A solution of 3-formyl-5,6-dihydro-4H-benzo[c][1,2] diselenole (35d) (278 mg., 1 mmole) in dimethylformamide-ethanol (3:1) (100 ml.) was added to 0.1 M-aqueous sodium hydrogen selenide (50 ml., 5 mmoles) under nitrogen and the mixture heated at 80° for 2.5 hours. The mixture was diluted with water and extracted with benzene. The washed, dried extracts, on evaporation, gave a yellow crystalline residue which was chromatographed on a column of alumina (30 x 2.0 cm) with benzene-ether (6:1) as eluant. Evaporation of the yellow eluates afforded only starting material (235 mg., 85%).

(5) 1,6,6a-Triselenapentalene (41e).

The oil, prepared as described in section (IV) part (5), was extracted with hot acetonitrile (4 x 50 ml.) and the resulting solution filtered. 0.5 M-Aqueous sodium hydrogen selenide (50 ml., 25 mmoles) was added to this cooled solution under nitrogen. The mixture was swirled, diluted with water, and extracted with benzene. The washed, dried extracts, on evaporation gave a residue which was chromatographed on a column of alumina (30 x 2.0 cm) with benzene as eluant. Evaporation of the purple eluates gave a residue which, after rechromatography, afforded a brown crystalline solid (59 mg., 1.7%). Recrystallisation of the residue from acetonitrile gave 1,6,6a-triselenapentalene (41e) as dark olive-green prisms, m.p. 151-152°

(decomp.), M^+ at $^m/e$ 302 (100%), (Found C, 19.9; H, 1.3; Se, 79.4. $C_5H_4Se_3$ requires C, 20.0; H, 1.3; Se, 78.7%).

(6) Attempted preparation of 2,5-dimethyl-1,6,6a-triselenapentalene

Finely ground phosphorus pentaselenide (10.9 g., 24 mmoles) was added to a solution of heptane-2,4,6-trione (1.42 g., 10 mmoles) in chlorobenzene (100 ml.) and the mixture boiled for 6 hours. The cooled mixture was diluted with water and extracted with benzene. The washed, dried extracts, on evaporation, gave a residue which was chromatographed on a column of alumina (30 x 2.5 cm.) with benzene as eluant. Elution with benzene-ether (3:1) gave blue-green eluates which were evaporated and the residue, after rechromatography, gave a red crystalline solid (90 mg., 4.8%). Recrystallisation from cyclohexane afforded 2,6-dimethyl-4H-pyran-4-selenoketone (58) (34 mg., 1.8%) as red needles, m.p. 131-133° (lit.[100] 137-138°), M^+ at $^m/e$ 188 (100%). (Found: C, 45.1; H, 4.5. C_7H_8SeO requires C, 44.9; H, 4.3%). λ_{max} 202, 252.5, 384, 618(s) and 650 (log ϵ 3.97, 3.97, 4.21, 2.23 and 2.47). The N.M.R. spectrum (carbon disulphide) showed a singlet (6H) at δ 1.95 (2 + 6 - CH_3) and a singlet (2H) at δ 6.99 (3 + 5 - H).

VIII Preparation of 1,6-dithia-6a-selenapentalenes (32).

(1) 3,4-Dimethyl-1,6-dithia-6a-selenapentalene (32c).

Phosphorus pentasulphide (5 g., 22.5 mmoles) was added to a solution of a mixture of 3,4-dimethyl-1-thia-6,6a-diselenapentalene (42c) and 3,4-dimethyl-1,6-dithia-6a-selenapentalene (32c) (1.047 g.) in the ratio 3:2 in benzene (50 ml.), and the mixture boiled for 30 minutes. The red solution was filtered, evaporated, and the crystalline residue chromatographed on a column of alumina (30 x 2.5 cm.) with benzene as eluant. Evaporation of the red eluates gave a crystalline residue (507 mg., 54%) which, after recrystallisation from cyclohexane, afforded 3,4-dimethyl-1,6-dithia-6a-selenapentalene (32c)(453 mg., 48%) as red needles, identical (by N.M.R.) with a sample obtained as described in section (IV) part (3).

(2) 4,5-Dihydro-3H-benzo [cd]-1,6-dithia-6a-selenapentalene (32d).

Phosphorus pentasulphide (11.1 g., 50 mmoles) was added to a solution of a mixture of 4,5-dihydro-3H-benzo [cd]-1,6-dithia-6a-selenapentalene (32d), 4,5-dihydro-3H-benzo [cd]-1-thia-6,6a-diselenapentalene (42d) and 4,5-dihydro-3H-benzo [cd]-1,6,6a-triselenapentalene (41d) (1.15 g.) in the ratio 4:10:1 in benzene (50 ml.). The mixture was treated as described in part (1) above. Work up gave a crystalline residue (821 mg., 82%) which, after recrystallisation from cyclohexane, afforded 4,5-dihydro-3H-benzo [cd]-1,6-dithia-6a-selenapentalene (32d) (784 mg., 78%) as red needles, m.p. 90-92°, M^+ at $^m/_e$ 248 (100%), (Found: C, 39.1; H, 3.4. $C_8H_8SeS_2$ requires C, 38.9; H, 3.3%).

(3) 1,6-Dithia-6a-selenapentalene (32e).

Phosphorus pentasulphide (10 g.) was added to a solution of a mixture of 1-thia-6,6a-diselenapentalene (42e), 1,6-dithia-6a-

selenapentalene (32e), 3-formylmethylene-3H-1,2-diselenole (35e) and 3-formylmethylene-3H-1,2-thiaselenole ($_{43}$) (ca. 500 mg.) in benzene (50 ml.) and the mixture treated as described in part (1) above. Work up gave a crystalline residue which was shown by N.M.R. to be impure. The impure material was treated twice more with phosphorus pentasulphide as described. Work up gave a crystalline residue (ca. 300 mg.) which, after recrystallisation from cyclohexane, afforded 1,6-dithia-6a-selenapentalene (32e) as orange plates identical (by N.M.R.) with a sample characterised by Reid[99].

IX Condensation and exchange reactions.

(1) Dimethylthioformamide (2.1 ml., 25 mmoles) was added to a suspension of 3-ethyl-4-methyl-1,2-diselenolium perchlorate (28c) (1.693 g., 5 mmoles) in acetic anhydride (20 ml.) and the mixture boiled for 30 minutes. Excess ether was added to the cooled solution when a dark oil separated. The ether layer was decanted, washed, dried and evaporated. The residue was chromatographed on a column of alumina (25 x 2.5 cm.) with benzene as eluant. Evaporation of the initial red eluates and rechromatography of the residue gave a crystalline solid (200 mg., 17%) which, after recrystallisation from cyclohexane, afforded 3,4-dimethyl-1,6-dithia-6a-selenapentalene (32c) (173 mg., 15%) as red spars, identical (by N.M.R.) with a sample obtained as described in section (IV) part (3).

(2) 3-(2-Dimethylamino-1-methylvinyl)-4-methyl-1,2-diselenolium perchlorate (29c) (1.968 g., 5 mmoles), when treated as described in part (1) above, afforded 3,4-dimethyl-1,6-dithia-6a-selenapentalene (32c) (212 mg., 18%) which recrystallised from cyclohexane as red spars, identical (by N.M.R.) with a sample obtained as described in section (IV)

part (3).

(3) 3-Methyl-5-phenyl-1,2-diselenolium perchlorate (1.933 g., 5 mmoles), when treated as described in part (1) above, gave no useful material.

(4) Dimethylthioformamide (0.4 ml., 5 mmoles) was added to a suspension of 3,4-dimethyl-1,6,6a-triselenapentalene (41c) (329 mg., 1 mmole) in acetic anhydride (4 ml.) and the mixture boiled for 30 minutes. The solution was diluted with water and extracted with benzene. The extracts were washed with water (twice), saturated potassium carbonate solution (once) and finally water (twice) before being dried and evaporated. The residue was chromatographed on a column of alumina (20 x 2.0 cm.) with benzene as eluant. Evaporation of the initial purple eluates gave a crystalline residue (53 mg.) shown by N.M.R. ($CDCl_3$) to be a mixture of 3,4-dimethyl-1,6,6a-triselenapentalene (41c), 3,4-dimethyl-1-thia-6,6a-diselenapentalene (42c) and 3,4-dimethyl-1,6-dithia-6a-selenapentalene (32c) in the ratio 1:3:1.

(5) Dimethylthioformamide (8.4 ml., 100 mmoles) was added to a suspension of tris (2-selenoformylcyclohexane-1-selenato) iron (III) (20d) (3.5g., 4.3 mmoles) in acetic anhydride (40 ml.) and the mixture boiled for 3 hours. Work up as described in part (4) above and chromatography with petrol-benzene (2:1) as eluant afforded mauve eluates which were evaporated and rechromatographed to give a crystalline solid (216 mg., 5.7%). Recrystallisation of the residue from methanol afforded 4,5-dihydro-3H-benzo [cd]-1-thia-6,6a-diselenapentalene (42d) (153 mg., 4.0%) as dark red needles, identical (by N.M.R.) with a sample prepared as described in section (VI) part (5).

(6) Phosphoryl chloride (2.3 ml., 25 mmoles) was added to a suspension of tris (2-selenoformylcyclohexane-1-selenato) iron (III) (20d) (3.5 g., 4.3 mmoles) in dimethylthioformamide (20 ml.) and the solution heated at 150° for 3 hours. Work up as described in part (4) above followed by chromatography on a column of silica (30 x 2.0 cm.) with benzene as eluant gave red eluates which were evaporated and the residue rechromatographed. The residual red oil (248 mg., 7.4%), which slowly crystallised, was recrystallised from methanol giving 4,5-dihydro-3H-benzo[cd]-1,6-dithia-6a-selenapentalene (32d) (168 mg., 5.2%) as red needles, identical (by N.M.R.) with a sample prepared as described in section (VIII) part (2).

(7) 3-(2-Dimethylamino-1-methylvinyl)-4-methyl-1,2-diselenolium perchlorate (29c) (1.968 g., 5 mmoles) was dissolved in thiolacetic acid (25 ml.) and the solution boiled for 30 minutes. Work up as described in part (4) above gave a purple crystalline solid (496 mg.,) which was shown by N.M.R. ($CDCl_3$) to be a 1:1 mixture of 3,4-dimethyl-1-thia-6,6a-diselenapentalene (42c) and 3,4-dimethyl-1,6-dithia-6a-selenapentalene (32c).

(8) Thiolacetic acid (4 ml.) was added to 3,4-dimethyl-1,6,6a-triselenapentalene (41c) (329 mg., 1 mmole) and the solution boiled for 30 minutes. Work up as described in part (4) above afforded 3,4-dimethyl-1,6-dithia-6a-selenapentalene (32c) (173 mg., 74%) identical (by N.M.R.) with a sample obtained as described in section (IV) part (3).

X Miscellaneous Reactions

(1) Preparation of 3,5-dimethyl-4H-selenopyran-4-selenoketone (36c).

See also section (VII) part (3,i).

(i) Phosphoryl chloride (0.55 ml., 6 mmoles) was added to a solution of

3,5-dimethyl-4H-selenopyran-4-one (49) (936 mg., 5 mmoles) in dry dimethylformamide (25 ml.). After 30 minutes, benzene was added immediately followed by a solution of potassium selenosulphate (3.57 g., 15 mmoles) in water (7.5 ml.) at 60°. The mixture was swirled for 1 minute, diluted with water, and extracted with benzene. Evaporation of the washed, dried extracts, shown by T.L.C. to be homogeneous, afforded 3,5-dimethyl-4H-selenopyran-4-selenoketone (36c) (610 mg., 49%) as a brown crystalline solid. Attempted methylation of the selenoketone with excess methyl iodide in both acetonitrile and benzene led only to black insoluble tars. The selenoketone could not be recrystallised because of its tendency to eliminate selenium.

(ii) In a second experiment, 3,5-dimethyl-4H-selenopyran-4-selenoketone (36c), prepared as above, was dissolved in benzene (500 ml.) and dry air was bubbled through the solution. After 5 hours there was no visible change in the dark green appearance, and T.L.C. showed a homogeneous solution. The solution was evaporated and left dry overnight. Chromatography of the residue on a column of silica (50 x 2.0 cm.), as described in section (VII) part (3,i), afforded 3,4-dimethyl-1,6-dioxa-6a-selenapentalene (48) (6 mg., 0.6%), 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole (35c) (169 mg., 13%) and 3,5-dimethyl-4H-selenopyran-4-one (49) (208 mg., 22%) all of which were identical (by T.L.C. or m.p.) with authentic samples.

(iii) In a third experiment, 3,5-dimethyl-4H-selenopyran-4-selenoketone (36c), prepared as described in part (i) above, was extracted with chloroform. The washed extract was allowed to stand in strong sunlight for 2 hours, dried and evaporated. Chromatography of the residue on a column of silica (50 x 2.0 cm.) as described in section (VII) part (3,i) afforded 3-(1-formylethylidene)-4-methyl-3H-1,2-diselenole (35c) (15 mg., 1.1%) and 3,5-dimethyl-4H-selenopyran-4-one (49) (360 mg., 38%) both identical

(by m.p.) with authentic samples.

(2) Reaction of 3,4-dimethyl-1,6-dioxa-6a-selenapentalene (48) with phosphorus pentasulphide.

3,4-Dimethyl-1,6-dioxa-6a-selenapentalene (48) (6 mg.) was boiled with phosphorus pentasulphide (ca. 100 mg.) in benzene (2 ml.) for 2 minutes. The mixture was diluted with water and extracted with benzene. Evaporation of the washed, dried extract gave a pink residue which was chromatographed on a column of alumina (10 x 1.0 cm.) with benzene as eluant. The pink eluates, on evaporation, afforded 3,4-dimethyl-1,6-dithia-6a-selenapentalene (32c) identical (by mass spectrum) with an authentic sample.

(3) Preparation of 3,5-dimethyl-4H-selenopyran-4-thione (63).

Phosphorus pentasulphide (2.22g., 10 mmoles) was added to a solution of 3,5-dimethyl-4H-selenopyran-4-one (49) (935 mg., 5 mmoles) in benzene (50 ml.) and the mixture boiled for 30 minutes. The cooled mixture was diluted with water, rinsing the flask out with 2M-aqueous sodium sulphide, and extracted with benzene. The washed, dried extracts were evaporated and the crystalline residue chromatographed on a column of alumina (30 x 2.5 cm.) with benzene as eluant. The initial pink eluates were rejected and the blue-brown dichroic fraction, on evaporation, gave a crystalline residue (953 mg., 94%) which, after recrystallisation from cyclohexane, afforded 3,5-dimethyl-4H-selenopyran-4-thione (63) (874 mg., 86%)as red needles, m.p. 109.5-110°, (Found: C,41.6; H,4.2. C_7H_8SeS requires C,41.4; H,4.0%).

(4) Attempted preparation of 3,4-dimethyl-6a-thia-1,6-diselenapentalene (62).

1M-Aqueous sodium hydroxide (10 ml., 10 mmoles) was added to a solution of sodium hydroxide (10 mmoles) in water (10 ml.) saturated with

hydrogen selenide (60 mmoles, from 6g. aluminium selenide) giving 0.5 M - sodium selenide (20 ml., 10 mmoles) as a slurry. This slurry of sodium selenide was immediately added to a solution of 3,5-dimethyl-4H-selenopyran-4-thione (63) (1.015 g., 5 mmoles) in dimethylsulphoxide (120 ml.) under nitrogen and the sodium selenide rinsed out with water (10 ml.). The resulting deep purple solution was stirred for 2 minutes, a layer of benzene was added, immediately followed by a solution of potassium ferricyanide (9.88 g., 30 mmoles) in water (30 ml.). The mixture was shaken, diluted with water, and extracted with benzene. The washed, dried extracts were evaporated and the residue chromatographed on a column of alumina (30 x 2.5 cm.) with benzene as eluant. An initial pale red fraction gave no useful material. Continued elution gave green-purple dichroic eluates which, on evaporation, afforded recovered starting material (641 mg., 63%).

(5) Attempted preparation of 4-methyl-5-(1-formylethylidene)-5H-1,2-thiaselenole (66).

A solution of mercury(II) chloride (272 mg., 1 mmole) in ethanol (10 ml.) was added to a solution of 3,5-dimethyl-4H-selenopyran-4-thione (203 mg., 1 mmole) in ether (20 ml.). The resulting yellow crystalline complex was filtered off, washed with ethanol, then ether, and dried. 0.5 M-Aqueous sodium carbonate (2 ml., 1 mmole) was added to a solution of the complex in dimethylsulphoxide (22 ml.) with swirling. After 10 minutes, the mixture was diluted with water and extracted with benzene. The washed, dried extracts were evaporated and the residue chromatographed on a column of alumina (30 x 2.0 cm.) with benzene as eluant. Evaporation of the green-brown dichroic eluates afforded only recovered starting material (69 mg., 34%).

(6) Self-condensation of 3-methyl-5-phenyl-1,2-diselenolium perchlorate (28b).

(i) 3-Methyl-5-phenyl-1,2-diselenolium perchlorate (28b) (1.933 g., 5 mmoles) was suspended in acetic anhydride (20 ml.) and dimethylthioformamide (1.1 ml., 12.5 mmoles) was added. The mixture was shaken and left overnight. The deep purple precipitate was filtered off and chromatographed on a column of alumina (30 × 3.6 cm.) with benzene as eluant. The deep purple eluates were evaporated and the residue, after rechromatography, gave a crystalline solid (581 mg.) which recrystallised from benzene as deep purple needles (457 mg.). The mass spectrum of this material showed it to be a mixture of 4-phenyl-6-methyl-2-selenaphenacylidene-2H-selenopyran (67) (and / or the 6-phenyl-4-methyl isomer), M^+ at $^m/_e$ 416, $C_{20}H_{16}Se_2$, and an analogous compound with one selenium atom replaced by a sulphur atom, M^+ at $^m/_e$ 368, $C_{20}H_{16}SeS$.

(ii) Triethylamine (1.4 ml., 10 mmoles) was added to a solution of 3-methyl-5-phenyl-1,2-diselenolium perchlorate (28b) (1.93 g., 5 mmoles) in acetonitrile (50 ml.). After 30 minutes, the mixture was diluted with water and extracted with benzene. The washed, dried extracts were evaporated and the residue chromatographed as described above in part (6, i). Recrystallisation of the residue (719 mg., 70%) from acetonitrile afforded 4-phenyl-6-methyl-2-selenaphenacylidene-2H-selenopyran (67) (and the 6-phenyl-4-methyl isomer) (451 mg., 44%) as deep purple needles, m.p. 185-190° and 221°, M^+ at $^m/_e$ 416 (100%), (Found: C, 58.3; H, 4.1. $C_{20}H_{16}Se_2$ requires C, 58.0; H, 3.9%). λ_{max} 215(s), 224(s), 237, 264, 372 and 540 (log ϵ 4.41, 4.41, 4.44, 4.46, 4.03, and 4.20). An N.M.R. spectrum could not be obtained because of the compound's insolubility.

(7) Attempted self-condensation of 3,5-dimethyl-1,2-diselenolium perchlorate (28a).

3,5-Dimethyl-1,2-diselenolium perchlorate (28a) (1.623 g., 5 mmoles) gave no useful material when reacted as described in part (6, ii) above.

(8) Condensation of tris (4-thiolopent-3-ene-2-thione) iron (III) (72) with dimethylthioformamide.

Tris (4-thiolopent-3-ene-2-thione) iron (III) was prepared from bis (3,5-dimethyl-1,2-dithiolium) tetrachloroferrate(II) (26) in 84% yield by reduction with sodium borohydride[112,113].

Phosphoryl chloride (3.5 ml., 37.5 mmoles) was added to a suspension of tris (4-thiolopent-3-ene-2-thione) iron (III) (72) (2.245 g., 5 mmoles) in dimethylthioformamide (25 ml.) and the mixture heated to 100° over 15 minutes. Excess ether was added to the cooled solution and the mixture was cooled at 0° for 30 minutes. The ether was decanted and the residual oil washed with ether. This procedure, dissolving the oil in dimethylformamide (25 ml.) and adding excess ether, was repeated 4 times to remove dimethylthioformamide. 2M-Aqueous sodium hydrogen sulphide (75 ml., 150 mmoles) was added to a filtered solution of the oil in dimethylformamide-ethanol (1:1) (100 ml.). The mixture was swirled, diluted with water and extracted with benzene. The washed, dried extracts, on evaporation, gave a dark red semi-crystalline solid which, after trituration with benzene, was filtered off giving a crystalline solid (150 mg., 5.1%). Recrystallisation from benzene afforded 2-(2'-dimethylaminovinyl)-4H-thiopyran-4-thione (74) (77 mg., 2.6%) as deep red prisms, m.p. 170-173° (decomposition), M^+ at $^m/_e$ 197 (100%), (Found: C, 55.1; H, 6.0; N, 6.9. $C_9H_{11}NS_2$ requires C, 54.8; H, 5.6; N, 7.1%). λ_{max} 205, 275(s), 284,

293.5, 356.5, 432, 518(s), 596(s) and 611(s). Log ϵ values could not be calculated as the compound decomposed. The N.M.R. spectrum ($CDCl_3$, 100 MHz) showed a singlet (6H) at δ 2.96 (NMe_2), a doublet (1H) at δ 5.01 ($J_{1',2'}$ = 13.4 Hz) (1'-H), a doublet (1H) at δ 7.10 ($J_{2',1'}$ = 13.4 Hz) (2'-H), a multiple doublet (1H) at δ 7.12 ($J_{6,5}$ = 9.4 Hz) (6-H), a double doublet (1H) at δ 7.54 ($J_{5,6}$ = 9.4 Hz and $J_{5,3}$ = 1.2 Hz) (5-H), and a singlet (1H) at δ 7.59 (3-H). One peak of the doublet at δ 7.10 coincides with one peak of the multiple doublet at δ 7.12 and the singlet at δ 7.59 obscures one peak of the double doublet at δ 7.54. In $CDCl_3$-C_6D_6 (ca. 1:1) the N.M.R. spectrum (100 MHz) showed a singlet (6H) at δ 2.43 (NMe_2), a doublet (1H) at δ 4.76 ($J_{1',2'}$ = 13.6 Hz) (1'-H), a doublet (1H) at δ 6.64 ($J_{6,5}$ = 9.9 Hz) (6-H), a doublet (1H) at δ 6.76 ($J_{2',1'}$ = 13.6 Hz) (2'-H), a double doublet (1H) at δ 7.50 ($J_{5,6}$ = 9.9 Hz and $J_{5,3}$ = 1.2 Hz) (5-H), and a broad singlet (1H) at δ 7.63 (3-H).

(9) Preparation of 2-(2'-dimethylaminovinyl)-4H-thiopyran-4-thione (74) from 2-methyl-4H-thiopyran-4-thione.

Phosphoryl chloride (0.2 ml., 2.5 mmoles) was added to a solution of 2-methyl-4H-thiopyran-4-thione (142 mg., 1 mmole) in dimethylthioformamide (2 ml.) and the mixture was heated to 100° over 15 minutes. The mixture was diluted with water, neutralised with sodium carbonate and extracted with benzene. The washed, dried extracts were evaporated and 2-(2'-dimethylaminovinyl)-4H-thiopyran-4-thione (15 mg., 7.6%) was filtered off, identical (by mass spectrum) with a sample prepared as described in part (8) above.

XI The Rearrangement of 6a-thiathiophthenes and 3-acylmethylene-3H-1,2-dithioles by nucleophiles.

3,4-Dimethyl-[18], 3,4-diphenyl-[15], 2-phenyl-, 2-t-butyl-[114], and 4-methyl-2-phenyl-6a-thiathiophthenes were prepared according to established procedures[24]. 4,5-Dihydro-3H-benzo[cd]-6a-thiathiophthene was prepared as described by Dingwall[15] and 6a-thiathiophthene was prepared from 4H-thiopyran-4-thione[27,28].

3-Formylmethylene-5-phenyl-, 3-(1-formylethylidene)-5-phenyl-, and 3-formylmethylene-5-t-butyl-3H-1,2-dithioles were prepared as described by Dingwall, McKenzie and Reid[24].

The following 4H-thiopyran-4-thiones used and described in this section were synthesised from the Vilsmeier salts:[29] 3,5-dimethyl-[18], 3,5-diphenyl-,2-phenyl-[4], 2-t-butyl-[114] and 5-methyl-2-phenyl-. 4H-Thiopyran-4-thione was prepared as described by Traverso[26].

In the preparation of 6a-thiathiophthene using the reaction sequence: tetrahydro-1,4-thiopyranone ⟶ 1-thiopyran-4-one ⟶ 1-thiopyran-4-thione[26,45] ⟶ 6a-thiathiophthene[27,28], the intermediate compounds were not recrystallised. Work up in the final reaction gave a red fraction which eluted before 6a-thiathiophthene during chromatography. This fraction was evaporated and the residue rechromatographed on a column of alumina (60 x 1.5 cm.) with petrol as eluant. Evaporation of the red eluates afforded a crystalline solid (31 mg.) which, after recrystallisation from petrol, gave 2-chloro-6a-thiathiophthene as red needles, m.p. 78 - 78.5°, M^+ at $^m/_e$ 196 (Cl isotope 37), (Found: C 31.2; H, 1.7. $C_5H_3S_3Cl$ requires C, 30.8; H, 1.6%), λ_{max} 198.5, 234.5, 258 and 487 nm., (log ϵ 4.19, 4.32, 4.66 and 3.66). The N.M.R. spectrum ($CDCl_3$)

showed a doublet (1H) at δ 8.19 ($J_{4,5}$ = 6.1 Hz) (4-H), a singlet (1H) at δ 9.11 (3-H) and a doublet (1H) at δ 9.16 ($J_{5,4}$ = 6.1 Hz) (5-H).

Preparation of 3-formyl-5,6-dihydro-4H-benzo[c][1,2] dithiole (87d).

Phosphoryl chloride (1.3 ml. 14 mmoles) was added to a solution of benzo [c][1,2] dithiolium perchlorate[15] (1.283 g., 5 mmoles) in dimethylthioformamide (10 ml.) and the solution warmed at 60° for 10 minutes. Dimethylformamide (50 ml.) was added and the solution cooled to 0°. 2M-Aqueous sodium hydroxide (60 ml., 120 mmoles) was added with swirling, the mixture was diluted with water, acidified with dilute hydrochloric acid, and extracted with benzene. The washed, dried extracts were evaporated and dimethylthioformamide was distilled from the oil at 0.1 mm. and 100°. The crystalline residue was chromatographed on a column of silica (25 x 2.5 cm.) with benzene as eluant. Evaporation of the initial red eluates and rechromatography of the residue gave a crystalline solid (157 mg., 16%) which, after recrystallisation from cyclohexane afforded 4,5-dihydro-3H-benzo [cd]-6a-thiathiophthene (89d) as red plates m.p. 80° (lit[15] m.p. 80°). Continued elution with benzene-ether (1:1) gave orange eluates which were evaporated and the residue rechromatographed on a column of silica (50 x 2.6 cm.) with benzene-ether (4:1) as eluant. Evaporation of the orange eluates (300 ml.) gave a crystalline solid (574 mg., 62%) which, after recrystallisation from cyclohexane, afforded 3-formyl-5,6-dihydro-4H-benzo [c][1,2] dithiole (87d) as yellow needles, m.p. 104°, (Found: C, 52.4; H, 4.5. $C_8H_8S_2O$ requires C, 52.2; H, 4.3%), λ_{max} 209(s), 230, 280(s), 407(s), 428 and 448 nm., (log ϵ 3.84, 4.16, 2.99, 3.82, 4.03, and 3.99); ν (C=O) ($CHCl_3$) 1597 and 1588 cm^{-1}. The N.M.R. spectrum ($CDCl_3$) showed a quintet (2H) at δ 1.90 (J = 6.2 Hz) (5-CH_2), a quartet (4H)

centred at δ 2.78 (J = 6.4 Hz) (4+6-CH_2), a triplet (1H) at δ 7.53 ($J_{7,6-CH_2}$ = 1.2 Hz) (7-H) and a singlet (1H) at δ 9.34 (CHO).

(1) Rearrangement of 3-acylmethylene-3H-1,2-dithioles by sodium hydrogen sulphide.

2M-Aqueous sodium hydrogen sulphide (5 ml., 10 mmoles) was added to a solution of the 3-acylmethylene-3H-1,2-dithiole (1 mmole) in dimethylformamide (DMF) (20 ml,) or dimethylformamide-ethanol (5:3) (DMF-EtOH) (20 ml.) at a specified temperature. After reaction, the mixture was diluted with water, acidified with dilute hydrochloric acid, and extracted with benzene. The washed, dried extracts were evaporated and the residue chromatographed on a column of alumina eluting initially with benzene. The 6a-thiathiophthene eluted quickly with benzene. Elution with a low percentage of ether in benzene gave the corresponding 4H-thiopyran-4-thione, and elution with benzene-ether (1:1) gave eluates containing recovered starting material. The yields quoted in this section are of T.L.C. pure crystalline material. Products were identified by comparative T.L.C. with authentic samples. In the case of runs which were not 1 mmole, the proportions were scaled up or down as appropriate.

3-Acylmethylene 3H-1,2-Dithiole		Scale mmole	Temp °C	Time	% Yield of Products 6a-Thiathiophthene	4H-Thiopyran -4-Thione	Recovered Aldehyde
		0.5	-10	5 hr	5	58	35
		2	0	5 hr	1	90	5
87a	(a)	0.5	20	10 min	-	43	50
		0.5	20	75 min	-	98	-
		0.5	40	30 min	-	89	-
	(a)	1	20	3 days	39	-	41
	(a)	1	20	7 days	36	-	29
87d	(a)	1	40	7 hr	36	-	41
	(a)	1	60	6 hr	40	-	17
	(a)	1	80	3 hr	59	-	4
	(b)	2	80	3 hr	81	-	5
		5	0	7 days	3	39	50
		5	20	3.5 days	4	67	22
87b	(b)	1	20	1 day	8	14	74
		1	40	1 day	4	74	16
		1	60	6 hr	4	81	10
		1	80	3 hr	5	87	2
		1	0	9 hr	3	28	-
		1	20	4 hr	3	50	-
87c	(b)	1	40	45 min	4	47	-
		1	60	15 min	4	49	-
		1	80	15 min	2	48	-

(a) solvent:- dimethylformamide

(b) solvent:- dimethylformamide-ethanol (5:3)

(2) Rearrangement of 6a-thiathiophthenes by sodium hydrogen sulphide.

2M-Aqueous sodium hydrogen sulphide (10 ml., 20 mmoles) was added to a solution of the 6a-thiathiophthene (2 mmoles) in dimethylformamide (DMF) (40 ml.) or dimethylformamide-ethanol (DMF-EtOH) (5:3) (40 ml.) at 20°. After reaction, the mixture was diluted with water and extracted with benzene. The washed, dried extracts were evaporated and the residue chromatographed on a column of alumina (35 x 2.0 cm.) with benzene as eluant. Unreacted 6a-thiathiophthene eluted quickly with benzene and the 4H-thiopyran-4-thione eluted with benzene-ether (4:1). The yields quoted

in this section are of T.L.C. pure crystalline material and products were identified by comparative T.L.C..

6a-Thiathiophthene	Solvent	Time	% Yield of Products: Recovered 6a-Thiathiophthene	% Yield of Products: 4H-Thiopyran-4-Thione
89a	DMF	2 hr	94	5
89c*	DMF-EtOH	4 hr	65	23
89b	DMF-EtOH	3.5 days	3	85

*2-Phenyl-6a-thiathiophthene precipitated from solution on addition of 2M-aqueous sodium hydrogen sulphide.

(3) Rearrangement of 6a-thiathiophthenes by sodium hydroxide.

2M-Aqueous sodium hydroxide (10 ml., 20 mmoles) was added to a solution of the 6a-thiathiophthene (2 mmoles) in dimethylformamide (DMF) (40 ml.) or dimethylformamide-ethanol (DMF-EtOH) (5:3) (40 ml.) at 70°. After 15 minutes the mixture was diluted with water and extracted with benzene. The washed, dried extracts were evaporated and the residue chromatographed on a column of alumina with benzene as eluant. Unreacted 6a-thiathiophthene eluted quickly with benzene. Elution with a low percentage of ether in benzene gave the corresponding 4H-thiopyran-4-thione and the 3-acylmethylene-3H-1,2-dithiole eluted with benzene-ether (1:1).

6a-Thiathiophthene	Solvent	% Yield of Products: Recovered 6a-Thiathiophthene	% Yield of Products: 4H-Thiopyran 4-Thione	% Yield of Products: 3-Acylmethylene 3H-1,2-Dithiole
89a	DMF	2	55	16
89d	DMF	36	-	19
89d	DMF-EtOH	44	-	35
89b	DMF	7	41	30

(4) Preparation of 4H-thiopyran-4-ones (93).

The 4H-thiopyran-4-thione was desulphurised to give the 4H-thiopyran-4-one by the method of Challenger and Mason[115]. A slurry of mercury (II) acetate (6.374 g., 20 mmoles) in acetic acid (12.5 ml.) was added to a solution of the 4H-thiopyran-4-thione (5 mmoles) in chloroform (25 ml.) and the mixture stirred for 24 hours. The mixture was filtered and the precipitate washed well with chloroform. The combined filtrate and washings were washed with water (twice), saturated potassium carbonate (once) and finally water (twice). The dried extracts were evaporated and the residue chromatographed on a column of alumina. The eluates were monitored for the 4H-thiopyran-4-one by T.L.C..

(i) 3,5-Dimethyl-4H-thiopyran-4-one (93f).

3,5-Dimethyl-4H-thiopyran-4-thione (780 mg., 5 mmoles) gave a residue which was chromatographed on a column of alumina (20 x 2.5 cm.) with benzene initially as eluant. Elution with benzene-ether (1:1) gave colourless eluates which, on evaporation, gave a white crystalline solid (591 mg., 84%). Recrystallisation of the residue from petrol afforded 3,5-dimethyl-4H-thiopyran-4-one (93f) (410 mg., 59%) as colourless needles, identical (by m.p.) with a sample prepared by Reid[99].

(ii) 3,5-Diphenyl-4H-thiopyran-4-one (93g).

3,5-Diphenyl-4H-thiopyran-4-thione (1.4 g., 5 mmoles) gave a residue which was chromatographed on a column of alumina (30 x 2.2 cm.) with benzene-ether (4:1) as eluant. Elution with benzene-ether (1:1) gave eluates which, on evaporation, gave a white crystalline solid (1.28 g., 97%). Recrystallisation of the residue from 5% benzene-cyclohexane afforded 3,5-diphenyl-4H-thiopyran-4-one (93g) (1.25 g., 95%) as colourless

needles, m.p. 173-174°, (Found C, 76.9; H, 4.5. $C_{17}H_{12}SO$ requires C, 77.2; H, 4.6%).

(iii) 2-Phenyl-4H-thiopyran-4-one (93c).

2-Phenyl-4H-thiopyran-4-thione (1.02 g., 5 mmoles) gave a residue which was chromatographed on a column of alumina (20 x 2.5 cm.) with ether as eluant. Elution with 2% ethanol-ether gave pale yellow eluates which were evaporated and the residue boiled with activated charcoal in acetonitrile. Evaporation of the filtrate gave a residue (926 mg., 99%) which, after recrystallisation from cyclohexane, afforded 2-phenyl-4H-thiopyran-4-one (93c) (718 mg., 76%) as colourless needles, m.p. 95-96° (lit[4] 94-96°), (Found: C, 70.1; H, 4.2. $C_{11}H_8SO$ requires C, 70.2; H, 4.3%).

(iv) 2-t-Butyl-4H-thiopyran-4-one (93b).

2-t-Butyl-4H-thiopyran-4-thione (920 mg., 5 mmoles) gave an oil which was chromatographed on a column of alumina (20 x 2.0 cm.) with ether as eluant. Elution with 2% ethanol-ether gave colourless eluates which, on evaporation, afforded an oil (829 mg., 99%) which crystallised on cooling. Recrystallisation of the residue from petrol gave 2-t-butyl-4H-thiopyran-4-one (93b) (717 mg., 85%) as fine colourless needles, m.p. 50-52°, (Found: C, 63.8; H, 6.9. $C_9H_{12}SO$ requires C, 64.2; H, 7.2%).

(v) 5-Methyl-2-phenyl-4H-thiopyran-4-one (93a).

5-Methyl-2-phenyl-4H-thiopyran-4-thione (1.09 g., 5 mmoles) gave a residue which was chromatographed on a column of alumina (30 x 2.0 cm.) with ether as eluant, An initial pale yellow fraction was rejected.

Elution with 2% ethanol-ether gave eluates which, on evaporation, afforded a crystalline residue (578 mg., 57%). Recrystallisation of the residue from cyclohexane gave 5-methyl-2-phenyl-4H-thiopyran-4-one (93a) (506 mg., 50%) as colourless prisms, m.p. 99-100°, (Found: C, 71.2; H, 5.0. $C_{12}H_{10}SO$ requires C, 71.2; H, 5.0%).

(vi) 4H-Thiopyran-4-one (93e).

4H-Thiopyran-4-one was prepared as described by Traverso[26].

(5) Preparation of quench calibration curves for 4H-thiopyran-4-ones.

An increasing weight of the 4H-thiopyran-4-one was approximately measured out into each of 12 volumetric flasks (25 ml.). Standard n-hexadecane-1-Cl4 solution (1.0 ml., 0.08514 μCi) was added to each and made up to the mark with scintillation mix. Each of these solutions (10.0 ml.) was pipetted into liquid scintillation vials and counted in counts per minute (c.p.m.). The efficiency of counting for each solution was calculated, knowing the disintegrations per minute (d.p.m.), and plotted against the external standard ratio.

(i) Quench calibration curve for 3,5-dimethyl-4H-thiopyran-4-one (93f).

Number	Ketone, mg.	C.P.M.	D.P.M.	Efficiency %	External Standard Ratio
1	0	57,221	75,600	75.7	12.46
2	5	55,041		72.8	10.80
3	11	53,987		71.4	10.27
4	16	54,810		72.5	10.77
5	21	53,530		70.8	10.32
6	25	51,628		68.3	9.23
7	32	52,398		69.3	9.58
8	40	48,372		64.0	8.14
9	51	46,096		61.0	7.62
10	62	46,122		61.0	7.80
11	71	42,583		56.3	6.74

(ii) Quench calibration curve for 3,5-diphenyl-4H-thiopyran-4-one (93g).

Number	Ketone, mg.	C.P.M.	D.P.M.	Efficiency %	External Standard Ratio
1	0	57,141	75,600	75.6	12.17
2	2.5	56,970		75.4	11.58
3	5	56,047		74.2	11.14
4	7.5	53,755		71.1	9.72
5	10	54,472		72.1	10.09
6	15	52,997		70.1	9.49
7	20	51,222		67.8	8.85
8	30	47,548		62.9	7.50
9	40	44,236		58.5	6.59
10	50	36,955		48.9	4.82
11	60	35,464		46.9	4.70
12	70	29,613		39.2	3.64

(iii) Quench calibration curve for 2-phenyl-4H-thiopyran-4-one (93c).

Number	Ketone, mg.	C.P.M.	D.P.M.	Efficiency %	External Standard Ratio
1	0	57,370	75,600	75.9	12.34
2	2.5	56,919		75.3	11.72
3	5	54,427		72.0	10.08
4	7.5	55,208		73.0	10.45
5	10	54,267		71.8	9.87
6	15	52,281		69.2	9.12
7	20	51,018		67.5	8.57
8	30	47,204		62.4	7.24
9	40	42,473		56.2	6.03
10	50	38,946		51.5	5.19
11	60	32,367		42.8	4.00
12	70	28,162		37.2	3.37

(iv) Quench calibration curve for 2-t-butyl-4H-thiopyran-4-one (93b).

Number	Ketone, mg.	C.P.M.	D.P.M.	Efficiency %	External Standard Ratio
1	0	57,104	75,600	75.5	12.03
2	2.5	56,911		75.3	11.74
3	5	56,173		74.3	11.49
4	7.5	56,309		74.5	11.37
5	10	55,429		73.3	11.21
6	15	54,833		72.5	10.62
7	20	54,464		72.0	10.32
8	30	52,636		69.6	9.62
9	40	50,965		67.4	8.96
10	50	49,130		65.0	8.24

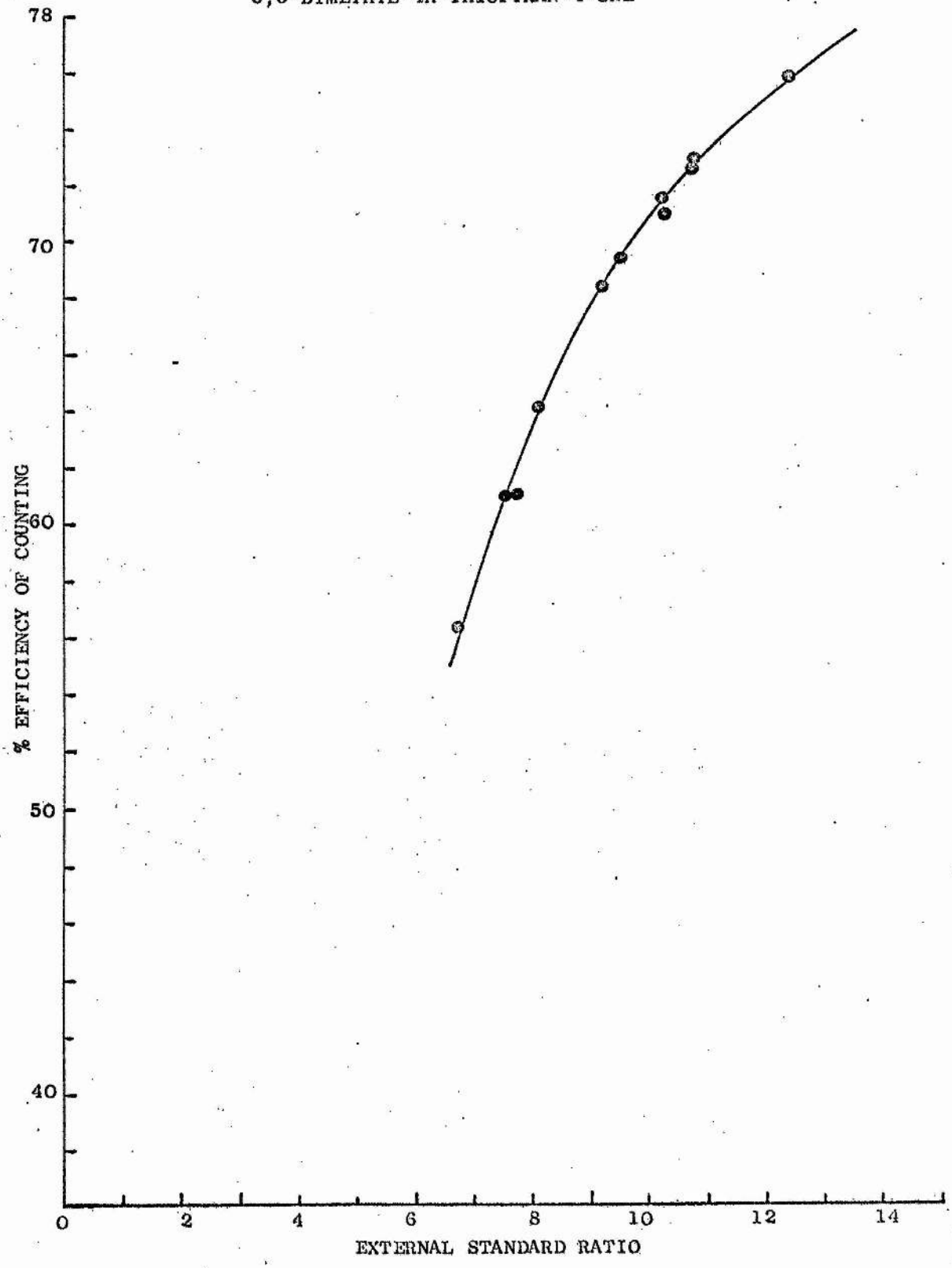
(v) Quench calibration curve for 5-methyl-2-phenyl-4H-thiopyran-4-one (93a)

Number	Ketone, mg.	C.P.M.	D.P.M.	Efficiency %	External Standard Ratio
1	0	57,351	75,600	75.9	12.16
2	2.5	56,850		75.2	11.53
3	5	56,211		74.4	10.97
4	7.5	55,128		72.9	10.42
5	10	54,280		71.8	9.96
6	15	52,633		69.6	9.35
7	20	50,592		66.9	8.47
8	30	46,099		61.0	6.89
9	40	43,390		57.4	6.47
10	50	37,792		50.0	5.12
11	60	36,186		47.9	4.89
12	70	30,400		40.2	4.01

(vi) Quench calibration curve for 4H-thiopyran-4-one (93 e).

Number	Ketone, mg.	C.P.M.	D.P.M.	Efficiency %	External Standard Ratio
1	0	56,024	75,600	74.1	11.29
2	2	55,432		73.3	10.68
3	5	55,731		73.7	11.25
4	11	54,489		72.1	10.46
5	21	50,475		66.8	8.51
6	33	48,546		64.2	8.23
7	41	43,781		57.9	6.89
8	50	40,518		53.6	6.15
9	58	39,480		52.2	5.92
10	70	34,289		45.4	4.95
11	82	30,397		40.2	4.34

QUENCH CALIBRATION GRAPH FOR
3,5-DIMETHYL-4H-THIOPYRAN-4-ONE



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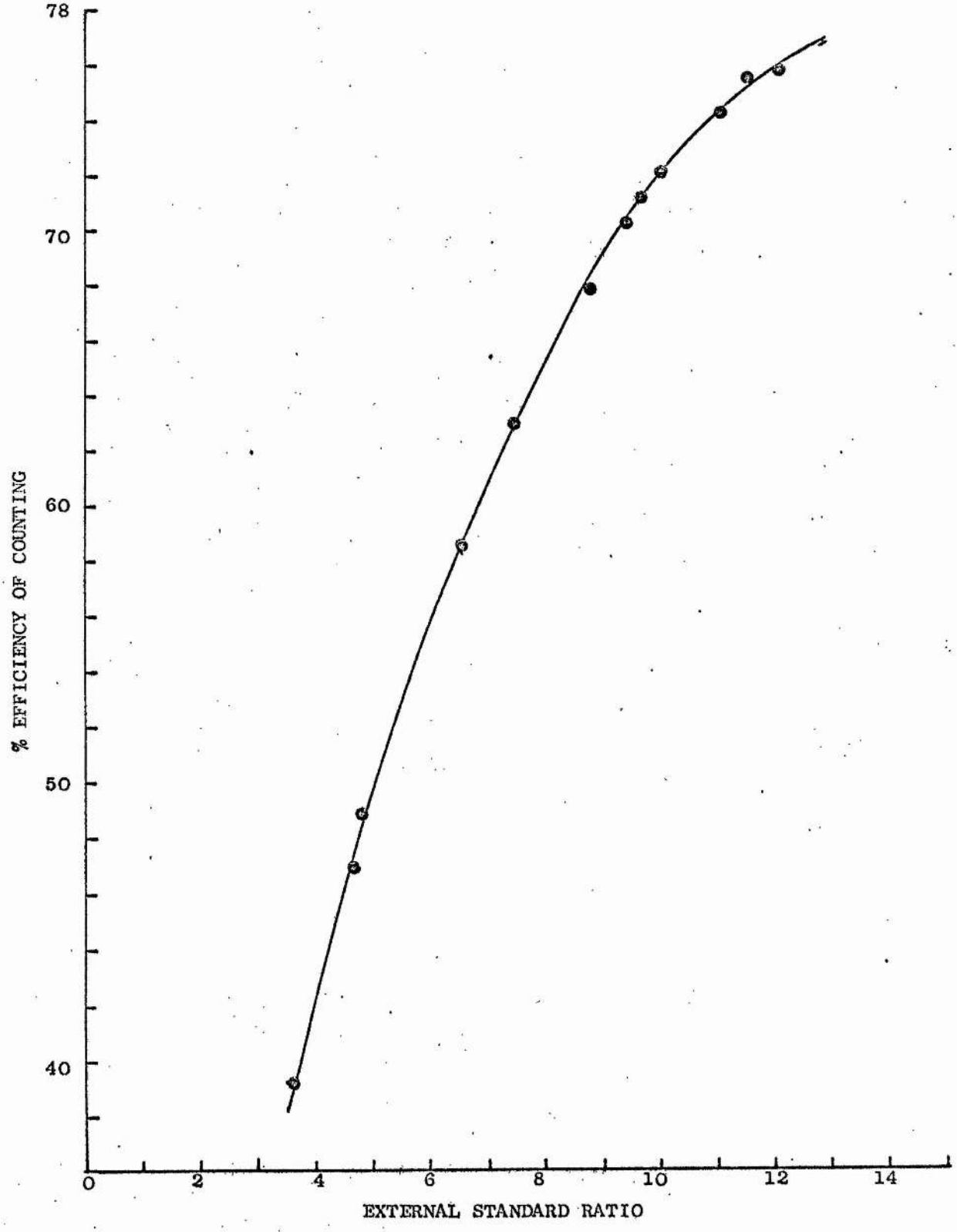
3,5-DIPHENYL-4H-THIOPYRAN-4-ONE



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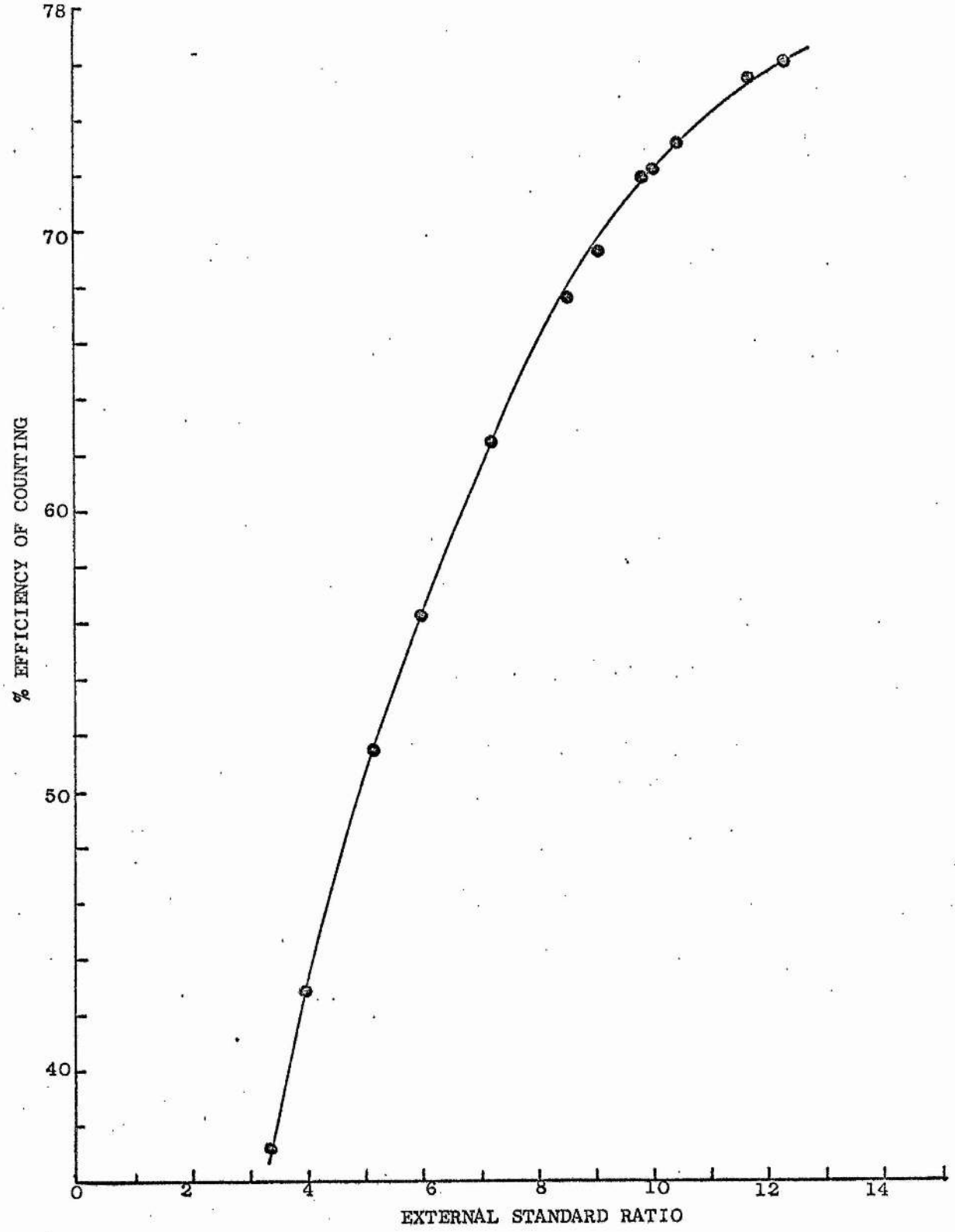
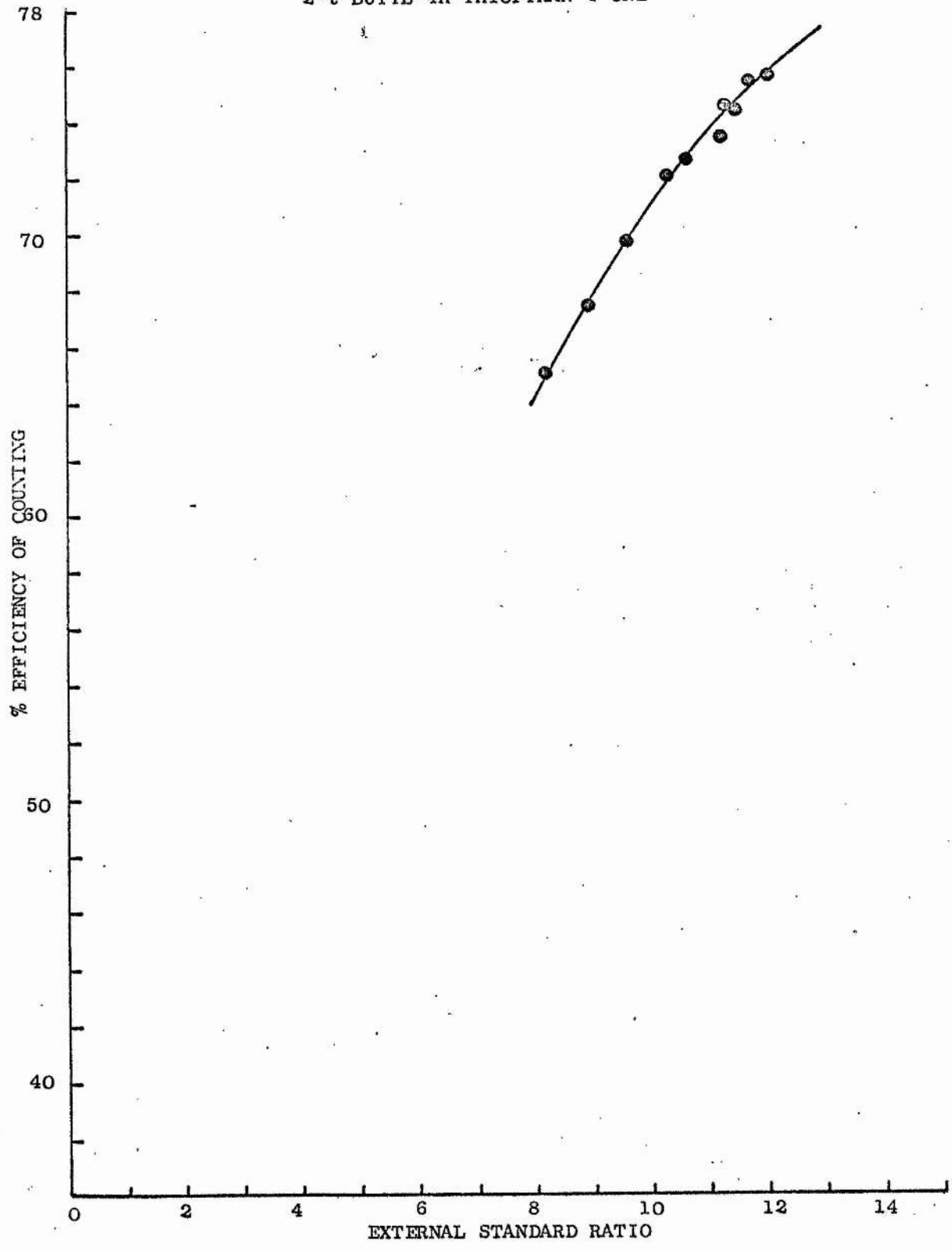
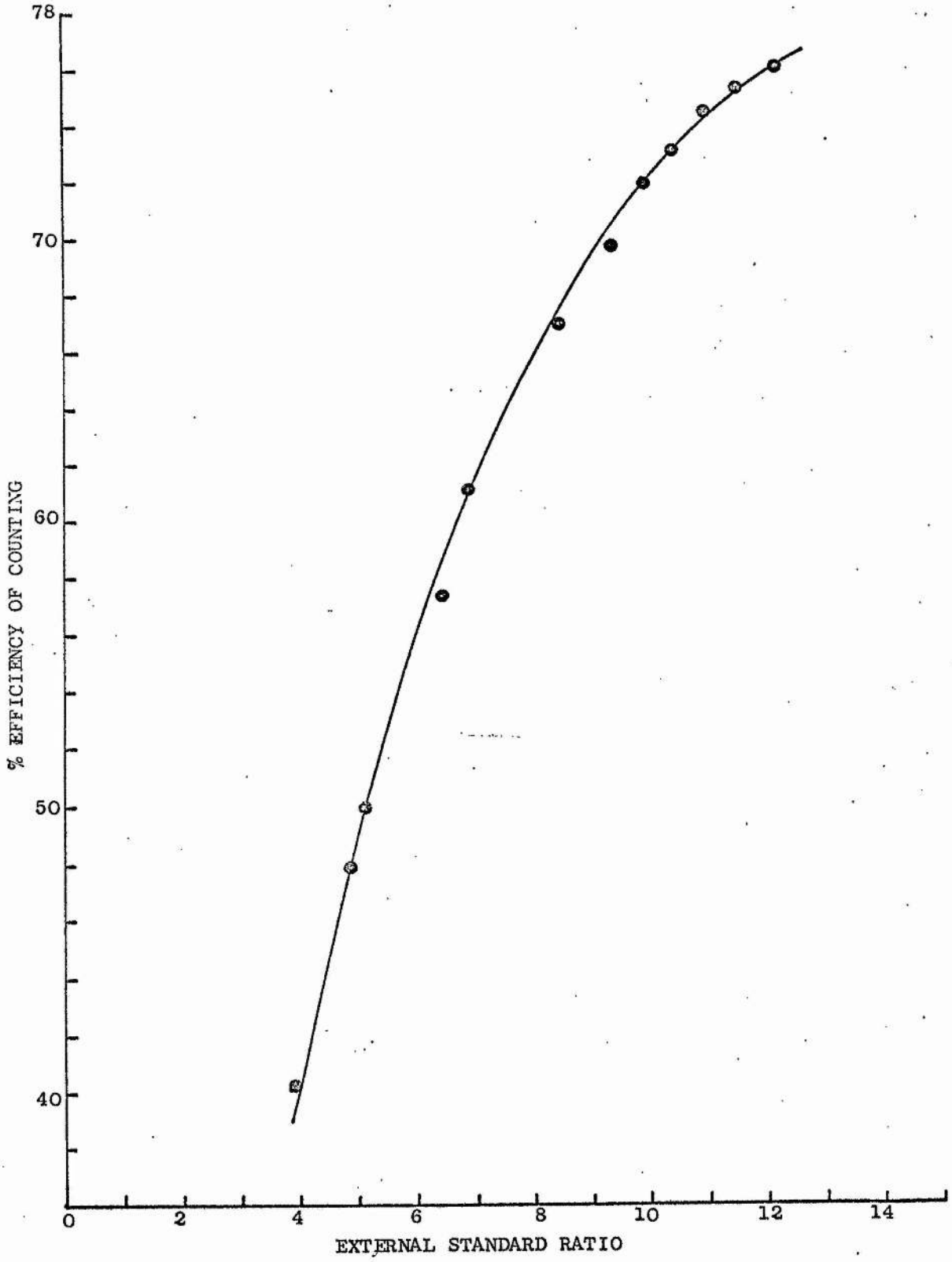
2-PHENYL-4H-THIOPYRAN-4-ONE



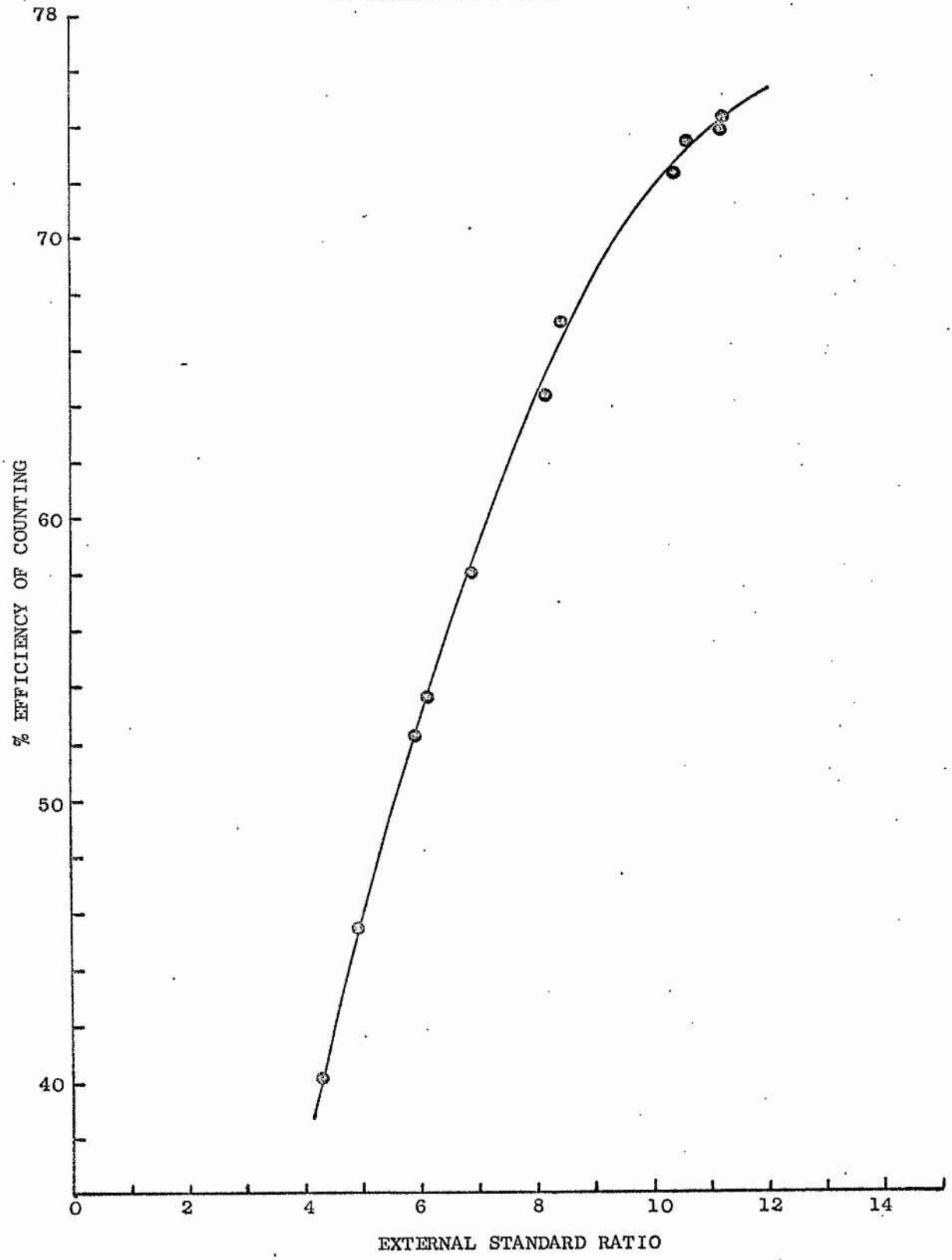
QUENCH CALIBRATION GRAPH FOR
2-t-BUTYL-4H-THIOPYRAN-4-ONE



QUENCH CALIBRATION GRAPH FOR
5-METHYL-2-PHENYL-4H-THIOPYRAN-4-ONE



QUENCH CALIBRATION GRAPH FOR
4H-THIOPYRAN-4-ONE.



(6) The Rearrangement of 6a-thiathiophthenes by aqueous sodium sulphide-S35.

1.6OM-Aqueous sodium sulphide-S35 (10 ml., 16 mmoles) was added to a solution of the thiathiophthene (2 mmoles) in dimethylformamide (40 ml.) at a specific temperature. After a given time the mixture was diluted with water and extracted with benzene. The washed, dried extracts were evaporated and the residue chromatographed on a column of alumina (30 x 2.0 cm.) with benzene as eluant. Unreacted thiathiophthene eluted quickly with benzene and was rejected. Continued elution with benzene or benzene-ether mixtures eluted the 4H-thiopyran-4-thione. These eluates were evaporated and the residue dissolved in chloroform (10 ml.). A slurry of mercury (II) acetate (2.55 g., 8 mmoles) in acetic acid (5 ml.) was added and the mixture stirred for 24 hours. Work up as described in part (4) for the 4H-thiopyran-4-one gave a residue which was chromatographed on a column of alumina (20 x 2.0 cm.). The 4H-thiopyran-4-one was eluted as described in the preparation (part 4). Evaporation of the colourless eluates gave a residue which was recrystallised and dried in a vacuum dessicator. Approximately 0.2 mmole of the 4H-thiopyran-4-one was weighed out accurately and transferred to a volumetric flask (25.0 ml.) which was then made up to the mark with scintillation mix. This solution (10.0 ml) was pipetted into a scintillation vial and counted. The efficiency of counting was determined by the external standard ratio from the quench calibration graph and hence the specific activity (μCi/mmole) of the 4H-thiopyran-4-one could be calculated. The specific activity (μCi /mmole) of the sodium sulphide-S35 solution was calculated for the day on which the 4H-thiopyran-4-one was counted knowing the half-life of S-35 and the time elapsed. The percentage incorporation of S-35 into the 4H-thiopyran-4-one, defined by the expression:-

$$\% \text{ incorporation} = \frac{\text{specific activity (4H-thiopyran-4-one)} \times 100}{\text{specific activity (sodium sulphide)}}$$

was calculated. The calculation for the rearrangement of 3,4-dimethyl-6a-thiathiophthene is given in appendix D and serves as an example.

(i) Rearrangement of 3,4-dimethyl-6a-thiathiophthene.

1.60M-Aqueous sodium sulphide-S35 (10 ml., 18.57 μCi, 1.1606 μCi/mmole) was added to a solution of 3,4-dimethyl-6a-thiathiophthene (376 mg., 2 mmoles) in dimethylformamide (40 ml.) and the mixture stood at 20° for 5 minutes. Work up as described gave 3,5-dimethyl-4H-thiopyran-4-thione (297 mg., 95%). Desulphurisation gave 3,5-dimethyl-4H-thiopyran-4-one (193 mg., 68%) which was recrystallised from petrol as colourless needles (93 mg.). The solution (10.0 ml) obtained by dissolving 3,5-dimethyl-4H-thiopyran-4-one (32.448 mg.) in scintillation mix (25.0 ml.) gave a count rate of 25,141 c.p.m. and an external standard ratio of 9.72. The efficiency of counting (69.7%) gave a specific activity of 0.1756 μCi /mmole of 3,5-dimethyl-4H-thiopyran-4-one, corresponding to an incorporation of sulphur-35 of 15.1% ± 1.1%.

(ii) Rearrangement of 3,4-diphenyl-6a-thiathiophthene.

1.60M-Aqueous sodium sulphide-S35 (10 ml., 11.622 μCi, 0.7264 μCi/mmole) was added to a solution of 3,4-diphenyl-6a-thiathiophthene (624 mg., 2 mmoles) in dimethylformamide (40 ml.). The mixture was swirled and immediately diluted with water. Work up as described gave 3,5-diphenyl-4H-thiopyran-4-thione (551 mg., 98%). Desulphurisation of the thione gave 3,5-diphenyl-4H-thiopyran-4-one (443 mg., 84%) which was recrystallised from cyclohexane as colourless needles (371 mg.). The solution (10.0 ml) obtained by dissolving 3,5-diphenyl-4H-thiopyran-4-one

(49.093 mg.) in scintillation mix (25.0 ml.) gave a count rate of 49,686 c.p.m. and an external standard ratio of 5.74. The efficiency of counting (53.9%) gave a specific activity of 0.559 μCi/mmole of 3,5-diphenyl-4H-thiopyran-4-one corresponding to an incorporation of sulphur-35 of 77.0% $\pm$ 5.4%.

(iii) Rearrangement of 2-phenyl-6a-thiathiophthene.

1.60M-Aqueous sodium sulphide-S35 (10 ml., 10.906 μCi, 0.6816 μCi/mmole) was added to a solution of 2-phenyl-6a-thiathiophthene (472 mg., 2 mmoles) in dimethylformamide (40 ml.) at 60°, and the mixture heated for 5 minutes. Work up as described gave 2-phenyl-4H-thiopyran-4-thione (240 mg., 59%). Desulphurisation of the thione in chloroform (5 ml.) by mercury(II) acetate (1.275 g., 4 mmoles) in acetic acid (2.5 ml.) afforded 2-phenyl-4H-thiopyran-4-one (173 mg., 46%) which was screened with activated charcoal and recrystallised from cyclohexane as colourless needles (104 mg.). The solution (10.0 ml) obtained by dissolving 2-phenyl-4H-thiopyran-4-one (29.933 mg.) in scintillation mix (25.0 ml.) gave a count rate of 10,797 c.p.m. and an external standard ratio of 6.89. The efficiency of counting (60.9%) gave a specific activity of 0.1256μCi/mmole of 2-phenyl-4H-thiopyran-4-one corresponding to an incorporation of sulphur-35 of 18.4% $\pm$ 1.3%.

(iv) Rearrangement of 2-t-butyl-6a-thiathiophthene.

1.60M-Aqueous sodium sulphide-S35 (10 ml., 10.314 μCi, 0.6446 μCi/mmole) was added to a solution of 2-t-butyl-6a-thiathiophthene (532 mg., 2 mmoles) in dimethylformamide (40 ml.) at 60° and the mixture heated for 5 minutes. Work up as described gave 2-t-butyl-4H-thiopyran-4-thione (339 mg., 92%). Desulphurisation of the thione afforded 2-t-butyl-4H-thiopyran

-4-one (302 mg., 90%) which was recrystallised from petrol as colourless needles (139 mg.). The solution (10.0 ml.) obtained by dissolving 2-t-butyl-4H-thiopyran-4-one (41.334 mg.) in scintillation mix (25.0 ml.) gave a count rate of 13,885 c.p.m. and an external standard ratio of 8.99. The efficiency of counting (67.8%) gave a specific activity of 0.09393 μCi/mmole of 2-t-butyl-4H-thiopyran-4-one corresponding to an incorporation of sulphur-35 of 14.6% ± 1.0%.

(v) Rearrangement of 4-methyl-2-phenyl-6a-thiathiophthene.

1.60M-Aqueous sodium sulphide-S35 (10 ml., 9.68 μCi, 0.605 μCi/mmole) was added to a solution of 4-methyl-2-phenyl-6a-thiathiophthene (500 mg., 2 mmoles) in dimethylformamide (40 ml.) at 60° and the mixture heated for 5 minutes. Work up as described gave 5-methyl-2-phenyl-4H-thiopyran-4-thione (400 mg., 92%). Desulphurisation of the thione gave 5-methyl-2-phenyl-4H-thiopyran-4-one (361 mg., 89%) which was recrystallised twice from cyclohexane as colourless prisms (260 mg.). The solution (10.0 ml.) obtained by dissolving 5-methyl-2-phenyl-4H-thiopyran-4-one (40.390 mg.) in scintillation mix (25.0 ml.) gave a count rate of 3,485 c.p.m. and an external standard ratio of 6.48. The efficiency of counting (58.1%) gave a specific activity of 0.03383 μCi/mmole of 5-methyl-2-phenyl-4H-thiopyran-4-one corresponding to an incorporation of sulphur-35 of 5.6% ± 0.4%.

(vi) Rearrangement of 6a-thiathiophthene.

1.60M-Aqueous sodium sulphide-S35 (25 ml., 42.88 μCi, 1.072 μCi/mmole) was added to a solution of 6a-thiathiophthene (800 mg., 5 mmoles) in dimethylformamide (100 ml.) at 60° and the mixture heated for 5 minutes.

The mixture was diluted with water, the aqueous layer neutralised, and extracted with benzene. Chromatography on a column of alumina (45 x 2.0 cm.) gave recovered 6a-thiathiophthene (153 mg., 19%) and 4H-thiopyran-4-thione (282 mg., 44%). Desulphurisation of the thione and chromatography eluting with 2% ethanol-ether afforded 4H-thiopyran-4-one (109 mg., 19%) which was recrystallised from carbon tetrachloride as colourless needles (39 mg.). The solution (10.0 ml) obtained by dissolving 4H-thiopyran-4-one (24.296 mg.) in scintillation mix (25.0 ml.) gave a count rate of 77,914 c.p.m. and an external standard ratio of 9.03. The efficiency of counting (68.1%) gave a specific activity of 0.5939 μCi / mmole of 4H-thiopyran-4-one corresponding to an incorporation of sulphur-35 of 55.3% $\pm$ 3.9%.

Summary of tracer results

6a-Thiathiophthene	Temp. °C	Time	4H-Thiopyran-4-one-S35	% Incorporation
3,4-dimethyl-	20	5 min	3,5-dimethyl-	15.1 $\pm$ 1.1
3,4-diphenyl-	20	immediate	3,5-diphenyl-	77.0 $\pm$ 5.4
2-phenyl-	60	5 min	2-phenyl -	18.4 $\pm$ 1.3
2-t-butyl-	60	5 min	2-t-butyl-	14.6 $\pm$ 1.0
4-methyl-2-phenyl-	60	5 min	5-methyl-2-phenyl-	5.6 $\pm$ 0.4
parent	60	5 min	parent	55.3 $\pm$ 3.9

APPENDIX A: N.M.R. SPECTRAL DATA

Solutions were in deuteriochloroform unless otherwise stated. Signals are singlets unless otherwise stated; b = broad, d = doublet, dd = double doublet, t = triplet, qt = quartet, qn = quintet, m = multiplet. J values are in Hz; δ values are in p.p.m. downfield from TMS.

* Denotes spectra recorded at 100 MHz.

Table A1: 2,4,6,8-Tetraselenaadamantanes(19).

Compound	Absorption
19a	1.96 (1 + 3 + 5 + 7 - CH_3), 1.99 (9 + 10 - CH_2).
	1.12t ($J_{CH_3CH_2}$ = 7.2)(1 + 3 - CH_3CH_2),
	1.33d ($J_{CH_3,9\text{-}H}$ = 6.5)(9 + 10 - CH_3),
19c	2.04 qt ($J_{CH_2CH_3}$ = 7.2)(1 + 3 - CH_3CH_2),
	ca. 2.3 bm (9 + 10 - H), 4.19 bm (5 + 7 - H).
19d	1.45 - 2.45 bm (1, 9 + 3, 10 - cyclohexane rings), 4.21 (5 + 7 - H).
19e	1.88 (1 + 3 - CH_3), 2.60 bt (9 + 10 - CH_2), 4.98 bm (5 + 7 - H).

Table A2: 1,2-Diselenolium perchlorates in trifluoroacetic acid solution

Compound	Absorption
28a	2.88 (3 + 5 - CH_3), 8.77 (4 - H).
28b	2.95 (3 - CH_3), 7.4 - 8.1 m (5 - Ph), 9.12 (4 - H).
28c	1.79 t ($J_{CH_3CH_2}$ = 7.2)(3 - CH_3CH_2), 2.80 (4 - CH_3), 3.06 qt ($J_{CH_2CH_3}$ = 7.2)(3 - CH_3CH_2), 11.10 (5 - H).

In tables 3, 4, and 5, the numbering of hydrogen atoms and substituents is related to the diagram shown below.

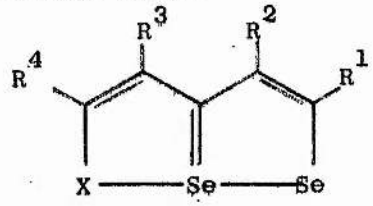


Table A3: 3-Acylmethylene-3H-1,2-diselenoles, x = O(35).

Compound	Absorption			
	R^4	R^3	R^2	R^1
35e [b]	9.44d	7.38d	8.00d	8.92d
	(J = 2.1)		(J = 6,7)	
35a	9.44d	7.23d	7.75	2.59
	(J = 2.0)			
35b	9.48d	7,36d	8.19	7.35 - 7.8[a]
	(J = 2.1)			
*35f [c]	10.20	2.58	10,10	7.35 - 7.95[a]
	10.29	2.52	10.00	7.35 - 7.95[a]
35c	9.27	2.42	2.70d	8.69b
			($J_{CH_3,5\text{-}H}$=1.0)	
31	2.31	2.38	2.65d	8.58b
			($J_{CH_3,5\text{-}H}$=1.0)	
35d	9.42	2,61t 1.92qt	2.90t	8,33
		($J_{4\text{-}CH_2,5\text{-}CH_2}$=5.8)	($J_{5\text{-}CH_2,6\text{-}CH_2}$ = 5.8)	

a Two multiplets (o and m + p proton signals).

b Spectrum of impure compound.

c Cis and trans isomers.

Table A4: 1-Thia-6,6a-diselenapentalenes, x = S (42).

Compound	Absorption			
	R^4	R^3	R^2	R^1
42e [b]	9.42d (J = 6.5)	8.32d	8.56d (J = 7.1)	10.32d
42a	9.40d (J = 6.5)	8.16d	8.35	2.70
42g	2.56	8.02	8.18	2.68
42b	9.38d (J = 6.5)	8.25d	8.76	7.3 - 7.9 [a]
*42f	10.38	2.68	10.11	7.3 - 8.0 [a]
42c [c]	9.20	2.86	2.94	10.12
42d	9.13t ($J_{3-CH_2,2-H}$=1.0)	2.9 - 3.3m	2.02m 2.9 - 3.3m ($J_{4-CH_2,5-H}$=1.0)	9.97t

a Two multiplets (o and m + p proton signals),

b 1:1 mixture with compound (32e).

c 2:1 mixture with compound (32c).

Table A5: 1,6,6a-Triselenapentalenes, x = Se (41).

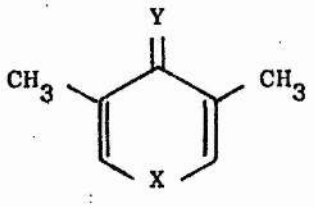
Compound	Absorption			
	R^4	R^3	R^2	R^1
*41e	10.41d (J = 6.9)	8.65d	8.65d (J = 6.9)	10.41d
*41a	2.60d ($J_{2-CH_3,3-H}$=0.8)	8.43b	8.49d (J = 6.9)	10.34d
41b	7.3 - 7.95 [a]	8.84	8.61d (J = 7.0)	10.35d
41f	7.35 - 8.0 [a]	10.17	2.70	11.08
*41c	10.21	2.95	2.95	10.21
*41d	10.07	3.11t 2.04qn ($J_{4-CH_2,5-CH_2}$=6.3)	3.11t ($J_{5-CH_2,6-CH_2}$=6.3)	10.07

a Two multiplets (o and m + p proton signals).

Table A6: 1,6-Dithia-6a-selenapentalenes (32).

Compound	Absorption			
	R^1	R^2	R^3	R^4
32e	9.45d (J = 6.7)	8.28d	8.28d (J = 6.7)	9.45d
*32c	9.20	2.90	2.90	9.20
*32d	9.05	3.05t ($J_{3\text{-}CH_2,4\text{-}CH_2}$ = 6.3)	2.00qn ($J_{4\text{-}CH_2,5\text{-}CH_2}$ = 6.3)	3.05t 9.05

Table A7: Data in this table is related to the diagram shown below.



Compound	X	Y	(2+6)-H	(3+5)-CH_3
36a	O	Se	7.87	2.37
36b	S	Se	7.86	2.68
36c	Se	Se	8.41	2.77
49	Se	O	7.94	2.19
63	Se	S	8.18	2.56

Table A8: 4H-Thiopyran-4-ones (93).

Compound	Absorption			
	R^1	R^2	R^3	R^4
93g	7.71	7.2-7.6m	7.2-7.6m	7.71
93a	7.52	7.22	2.21d ($J_{5\text{-}CH_3,6}$=1.0)	7.61d ($J_{6,5\text{-}CH_3}$=1.0)
93b	1.37	7.00d ($J_{3,5}$ = 1.4)	6.93dd ($J_{5,6}$ = 10.6) ($J_{5,3}$ = 1.4)	7.78d ($J_{6,5}$ = 10.6)
93c	7.52	7.21d ($J_{3,5}$ = 1.2)	7.04dd ($J_{5,6}$ = 10.4) ($J_{5,3}$ = 1.2)	7.81d ($J_{6,5}$ = 10.4)

Table A9: 4H-Thiopyran-4-ones in trifluoroacetic acid.

Compound	Absorption			
	R^1	R^2	R^3	R^4
93g	9.32	7.61	7.61	9.32
93a	7.78	8.38	2.68	9.18
93b	1.65	8.16d ($J_{3,5}$ = 1.4)	8.02dd ($J_{5,6}$ = 9.6) ($J_{5,3}$ = 1.4)	9.30d ($J_{6,5}$ = 9.6)
93c	7.80	8.33d ($J_{3,5}$ = 1.7)	8.15dd ($J_{5,6}$ = 9.7) ($J_{5,3}$ = 1.7)	9.35d ($J_{6,5}$ = 9.7)

APPENDIX B: ULTRA-VIOLET AND VISIBLE SPECTRAL DATA

Solutions were in cyclohexane unless otherwise stated, S = shoulder, b = very broad peak with no fine structure, log ϵ values are given under the absorption λ_{max}, nm,

Table B1: 2,4,6,8-Tetraselenaadamantanes (19).

Compound	Absorption			
19a	215	235,5	252,5S	305
	(4,01	3,66	3,43	3,24)
19c	216,5	238S	257S	306
	(3,99	3,57	3,38	3,26)
19d	205S 216,5	239S	256S	308
	(3,87 4,04	3,62	3,43	3,29)
19e	216		258	308
	(4,00		3,34	3,24)

Table B2: 1,2-Diselenolium perchlorates in 2% v/v perchloric acid-acetic acid.

28a	308S		325		
	(3,87		3,93)		
28b	250	280	334S	384	
	(3,68	3,35	3,87	4,25)	
28c	291		340		
	(3,77		3,82)		

Table B3: 3-Acylmethylene-3H-1,2-diselenoles (35).

Compound	Absorption								
35a	214S	232	249S	297				428S	446
	(4.11	4.38	3.96	3.27				4.02	4.18)
35b	214S	228	241S	297S		325			461
	(4.32	4.44	4.34	3.86		3.98			4.09)
35f		223	287			344			461
		(4.45	4.02			4.03			4.24)
35c	207	232	250S	309	387S		403S	448S	468
	(4.04	4.26	3.94	3.07	3.55		3.59	4.00	4.13)
3I	210S	229	249S	308	380S			445S	461
	(4.08	4.30	3.90	3.08	3.13			4.04	4.16)
35d	204	233	255S	300S				452S	469
	(4.13	4.29	3.95	2.94				4.01	4.10)

Table B4: 1-Thia-6,6a-diselenapentalenes (42).

42a	211	243	261	322		495	554S
	(4.26	4.57	4.70	3.57		3.87	3.05)
42g	215	247S	263	323		491	542S
	(4.37	4.58	4.70	3.62		3.93	3.25)
42b	209	250	274S		356	514	584S
	(4.41	4.77	4.40		4.03	3.99	3.09)
42f	211	238	263	315	367	504	
	(4.43	4.58	4.63	4.03	4.03	4.03)	
42d	203	242	266	317S		518	579S
	(4.33	4.52	4.61	3.35		3.80	3.14)

Table B5: 1,6,6a-Triselenapentalenes (41).

Compound	Absorption								
41e	203	215S	257S	272	322S	327S	378S	531	638
	(4,38	4,17	4,60	4,80	3,43	3,41	2,51	3,76	2,85)
41a	208			272,5		335		524	622
	(4,39			4,81		3,63		3,83	2,93)
41b	208	227S		267		367		540	643
	(4,40	4,33		4,78		4,05		3,98	3,06)
41f		217	249S	273	318S	372		529	646
		(4,43	4,51	4,70	4,06	4,06		3,95	2,72)
41c	208			270S	281			546	664
	(4,33			4,64	4,68			3,82	2,79)
41d	207	218S		265S	278	330S		545	654
	(4,41	4,20		4,62	4,71	3,41		3,80	2,97)

Table B6: 1,6-Dithia-6a-selenapentalenes (32).

32c	205S	220S	232	255,5	320S	491
	(4,10	4,34	4,54	4,47	3,15	3,84)
32d	198	217	232	255	320S	503
	(4,25	4,34	4,53	4,49	2,97	3,82)

Table B7: Miscellaneous Compounds

36a	206	236	254	383	613S	632	663S	672
	(3,89	3,65	3,71	4,13	2,04	2,14	2,29	2,31)
49	207	229	269	303S	307	314		
	(3,62	3,63	3,57	4,20	4,21	4,23)		
63	208	267,5	307	312,5S	388	600b		
	(4,12	3,43	3,16	3,15	4,39	1,39)		

APPENDIX C: INFRA-RED SPECTRAL DATA

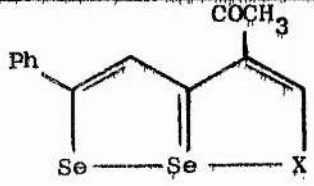
Solutions were in chloroform except where stated. Absorption data refers to the carbonyl stretching frequency ν C = O cm^{-1}.

S = shoulder, b = broad.

Table C1: 3-Acylmethylene-3H-1,2-diselenoles (35).

Compound	Absorption
35a	1575
35b	1565 1561S
35f	1648 (trans) 1511b (cis)
35c *	1564
31 *	1530
35d	1571

Table C2: Data here refers to the diagram shown below



Compound		Absorption
35f	X = O	1648 (trans), 1511b (cis)
42f	X = S	1664
41f	X = Se	1667

Table C3: 4H-Thiopyran-4-ones (93).

Compound	Absorption
2-phenyl-	1604
2-t-butyl-	1610
2-phenyl-5-methyl-	1596
3,5-diphenyl-	1608, 1594

* Denotes spectra recorded as a nujol mull.

APPENDIX D: DERIVATION OF FORMULAE AND CALCULATION OF THE SPECIFIC ACTIVITY OF 3,5-DIMETHYL-4H-THIOPYRAN-4-ONE AFTER THE REARRANGEMENT OF 3,4-DIMETHYL-6a-THIATHIOPHTHENE BY AQUEOUS SODIUM SULPHIDE - S35

Symbols:-

N = Number of μCi present after time T.

N_o = Initial number of μCi.

λ = Radioactive decay constant.

$T_{\frac{1}{2}}$ = Half-life of sulphur-35

$$-\frac{dN}{dT} = \lambda N$$

$$\ln N = -\lambda T + C$$

when $T = 0$, $N = N_o$

$$\therefore \quad C = \ln N_o$$

$$\therefore \quad \ln \frac{N}{N_o} = -\lambda T \qquad \ldots\ldots\ldots\ldots\ldots\ldots \text{ I}$$

at $T = T_{\frac{1}{2}}$, $N = \frac{N_o}{2}$

$$\therefore \quad \ln \tfrac{1}{2} = -\lambda T_{\frac{1}{2}}$$

$$\therefore \quad \lambda = \frac{\ln 2}{T_{\frac{1}{2}}}$$

for sulphur-35, $T_{\frac{1}{2}}$ is 87.2 days.

$$\therefore \quad \lambda = \frac{0.6931}{87.2} \text{ days}^{-1}$$

i.e. $\lambda = 7.949 \times 10^{-3} \text{ days}^{-1}$ for sulphur-35

From I, $\frac{N}{N_o} = e^{-\lambda T}$

$\log \frac{N}{N_o} = \log e^{-\lambda T}$

$\log \frac{N}{N_o} = -\lambda T \log e$

$\log N = \log N_o - \lambda T \log e$

here $N_o = 1160\ \mu Ci$

$\therefore \log N = \log 1160 - 7.949 \times 10^{-3} \times 0.4343\ T$

i.e. $\underline{\log N = 3.0645 - 3.452 \times 10^{-3}\ T}$

$\therefore$ The number of μ Ci of sulphur-35 and hence the specific activity of the sodium sulphide solution can be calculated after time T days.

The solution (10.0 ml) obtained by dissolving 3,5-dimethyl-4H-thiopyran-4-one (32.448 mg.) in scintillation mix (25.0 ml.) gave a count rate of 25,141 c.p.m. and an external standard ratio of 9.72.

∴ from the quench calibration graph, efficiency of counting = 69.7%.

c.p.m. = 25,141 in 10.0 ml.

d.p.m. = $25,141 \times \frac{100}{69.7}$ in 10.0 ml.

d.p.m. = $25,141 \times \frac{100}{69.7} \times \frac{25}{10}$ in 25.0 ml.

d.p.m. = $25,141 \times \frac{100}{69.7} \times \frac{25}{10} \times \frac{0.1403}{0.03245}$ per mmole.

∴ specific activity = $25,141 \times \frac{100}{69.7} \times \frac{25}{10} \times \frac{0.1403}{0.03245} \times \frac{1}{3.7 \times 10^4 \times 60 \mu Ci/mmole}$

since $1 \mu Ci = 3.7 \times 10^4 \times 60$ d.p.m.

i.e specific activity of 3,5-dimethyl-4H-thiopyran-4-one = 0.1756 μCi/mmole

here T = 28 days

∴ log N = $3.0645 - 3.452 \times 10^{-3} \times 28$

∴ log N = 2.9678

∴ N = 928.5 μCi

∴ sodium sulphide solution = 928.5 μCi/800 mmoles

i.e. specific activity = 1.1606 μCi/mmole

∴ incorporation of sulphur-35 = $\frac{0.1756 \times 100}{1.1606}$ %

i.e. incorporation of sulphur-35 into 3,5-dimethyl-4H-thiopyran-4-one = 15.1%

The estimated percentage error of the percentage incorporation of sulphur-35 is $\pm$ 7.0% of the values found in section (XI) part (6). Thus, the incorporation of sulphur-35 into 3,5-dimethyl-4H-thiopyran-4-one = 15.1 $\pm$ 1.1%.

REFERENCES

1. F. Arndt, P. Nachtwey, and J. Pusch, Ber., 1925, 58, 1633.
2. F. Arndt, R. Schwarz, C. Martius, and E. Aron, Rev.Fac.Sci.Univ. Istanbul Ser. C, 1948, A13, 57; Chem. Abstracts, 1948, 42, 4176i.
3. G. Traverso and M. Sanesi, Ann.Chim. (Italy), 1953, 43, 795.
4. G. Traverso, Ann.Chim. (Italy), 1954, 44, 1018.
5. G. Traverso, Ann.Chim. (Italy), 1955, 45, 687.
6. G. Traverso, Ann.Chim. (Italy), 1956, 46, 821.
7. A.A. Bothner-By and G. Traverso, Chem.Ber., 1957, 90, 453.
8. S. Bezzi, M. Mammi, and C. Garbuglio, Nature, 1958, 182, 247.
9. S. Bezzi, C. Garbuglio, M. Mammi, and G. Traverso, Gazzetta, 1958, 88, 1226.
10. G. Guillouzo, Bull.Soc.chim. France, 1958, 1316.
11. D.S. Breslow and H. Skolnik, "Multi-Sulphur and Sulphur and Oxygen Five- and Six-Membered Heterocycles", Interscience, 1966, Part One, pp. 410-416.
12. N. Lozac'h and J. Vialle, "Chemistry of Organic Sulphur Compounds", ed. N. Kharasch and C.Y. Meyers, Pergamon Press, London, 1966, Vol.2 , pp. 276-280.
13. N. Lozac'h, "Organosulphur Chemistry", ed. M.J. Janssen, Interscience, New York, 1967, p. 179.
14. R.J.S. Beer, "Mechanisms of Reactions of Sulphur Compounds", ed. N. Kharasch, B.S. Thyagarajan,and A.I. Khodair, Intrascience Research Foundation, Santa Monica, California, 1968, Vol. 2, p. 121.
15. J.G. Dingwall, Ph.D. Thesis, University of St. Andrews, 1968.
16. W.G. Salmond, Quart.Rev., 1968, 22, 253.
17. E. Klingsberg, Quart.Rev., 1969, 23, 537.
18. J.D. Symon, Ph.D. Thesis, University of St. Andrews, 1970.
19. D.H. Reid, "Organic Compounds of Sulphur, Selenium, and Tellurium", ed. D.H. Reid, The Chemical Society, London, 1970, Vol.1, p. 321.

20. H, Behringer, M. Ruff, and R. Wiedenmann, Chem.Ber., 1964, 97, 1732.

21. G. Pfister-Guillouzo and N. Lozac'h, Bull.Soc.chim. France, 1963, 153.

22. M. Stavaux and N. Lozac'h, Bull.Soc.chim. France, 1967, 2082.

23. D. Leaver and W.A.H. Robertson, Proc.Chem.Soc., 1960, 252.

24. J.G. Dingwall, S. McKenzie, and D.H. Reid, J.Chem.Soc. (C), 1968, 2543.

25. J.G. Dingwall, D.H. Reid, and K. Wade, J.Chem.Soc.(C), 1969, 913.

26. G. Traverso, Chem.Ber., 1958, 91, 1224.

27. J.G. Dingwall, D.H. Reid, and J.D. Symon, Chem.Comm., 1969, 466.

28. J.G. Dingwall, D.H. Reid, and J.D. Symon, J.Chem.Soc.(C), 1970, 2412.

29. J.G. Dingwall and D.H. Reid, Chem.Comm., 1968, 863.

30. M. Mammi, R. Bardi, C. Garbuglio, and S. Bezzi, Acta Cryst., 1960, 13, 1048.

31. A. Hordvik, Acta Chem.Scand., 1966, 20, 1885.

32. A. Hordvik, E. Sletten, and J. Sletten, Acta Chem.Scand., 1969, 23, 1852.

33. A. Hordvik, E. Sletten, and J. Sletten, Acta Chem.Scand., 1966, 20, 2001.

34. S.M. Johnson, M.G. Newton, and I.C. Paul, J.Chem.Soc.(B), 1969, 986.

35. S.M. Johnson, M.G. Newton, I.C. Paul, R.J.S. Beer, and D. Cartwright, Chem.Comm., 1967, 1170.

36. A. Hordvik, Acta Chem.Scand., 1968, 22, 2397.

37. P.L. Johnson and I.C. Paul, Chem.Comm., 1969, 1014.

38. A. Hordvik, Acta Cryst., 25A, 1969, Part S3, 151.

39. A. Hordvik and K. Julshamn, Acta Chem.Scand., 1969, 23, 3611.

40. F. Leung and S.C. Nyburg, Chem.Comm., 1969, 137.

41. A. Hordvik and L.J. Saethre, Acta Chem.Scand., 1970, 24, 2261.

42. A. Hordvik and L. Hansen, Acta Chem.Scand., 1970, 24, 2246.

43. I.C. Paul, unpublished data.

44. H.G. Hertz, G. Traverso, and W. Walter, Annalen, 1959, 625, 43.

45. G. Pfister-Guillouzo and N. Lozac'h, Bull.Soc.chim. France, 1964, 3254.

46. R. Pinel, Y. Mollier, and N. Lozac'h, Bull.Soc.chim. France, 1967, 856.

47. M. Stavaux and N. Lozac'h, Bull.Soc.chim. France, 1968, 2077.

48. C. Trébaul and J. Teste, Bull.Soc.chim. France, 1966, 3790.

49. S. McKenzie and D.H. Reid, Chem.Comm., 1966, 401.

50. D.T. Clark, D. Kilcast, and D.H. Reid, Chem.Comm., 1971, 638.

51. F. Gerson, R. Gleiter, J. Heinzer, and H. Behringer, Angew.Chem. Internat.Edn., 1970, 9, 306.

52. R. Gleiter and R. Hoffmann, Tetrahedron, 1968, 24, 5899.

53. H. Yamabe, H. Kato, and T. Yonezawa, Bull.Chem.Soc. Japan, 1970, 43, 3754.

54. R. Gleiter, D. Schmidt, and H. Behringer, Chem.Comm., 1971, 525.

55. S. Pietra, C. Garbuglio, and M. Mammi, Gazzetta, 1964, 94, 48.

56. R. Pinel, Y. Mollier, and N. Lozac'h, Bull.Soc.chim. France, 1966, 1049.

57. M. Sanesi and G. Traverso, Chem.Ber., 1960, 93, 1566.

58. M. Sanesi, G. Traverso, and M. Lazzarone, Ann.Chim. (Italy), 1963, 53, 548.

59. G. Giacometti and G. Rigatti, J.Chem.Phys., 1959, 30, 1633.

60. E.M. Shustorovich, Zhur.obshchei Khim., 1959, 29, 2459; Chem.Abstracts, 1960, 54, 8269f.

61. K. Maeda, Bull.Chem.Soc. Japan, 1960, 33, 1466.

62. K. Maeda, Bull.Chem.Soc. Japan, 1961, 34, 785.

63. K. Maeda, Bull.Chem.Soc. Japan, 1961, 34, 1166.

64. R.J. Hach and R.E. Rundle, J.Amer.Chem.Soc., 1951, 73, 4321.

65. R. Daudel and O. Chalvet, J.Chem.Phys., 1956, 53, 943.

66. R.A,W. Johnstone and S.D. Ward, Theor.Chim.Acta , 1969, 14, 420.

67. J.H. van den Hende and E. Klingsberg, J.Amer.Chem.Soc., 1966, 88, 5045.

68. E.E. Havinga and E.H. Wiebenga, Rec.Trav.chim., 1959, 78, 724.

69. D. Leaver and D.M. McKinnon, Chem. and Ind., 1964, 461.

70. M. Mammi, R. Bardi, G. Traverso, and S. Bezzi, Nature, 1961, 192, 1282.

71. L. Pauling, "The Nature of the Chemical Bond", 3rd edn., Cornell Univ. Press, Ithaca, New York, 1960.

72. J.A. Kapecki and J.E. Baldwin, J.Amer.Chem.Soc., 1969, 91, 1120.

73. E. Klingsberg, J.Org.Chem., 1966, 31, 3489.

74. H. Behringer and D. Weber, Chem.Ber., 1964, 97, 2567.

75. Y. Mollier, F. Terrier, and N. Lozac'h, Bull.Soc.chim. France, 1964, 1778.

76. D. Festal and Y. Mollier, Tetrahedron Letters, 1970, 1259.

77. I.H. Pomerantz and L.J. Miller, Quart.Reports Sulphur Chem., 1970, 5, 233.

78. H. Behringer and D. Bender, Chem.Ber., 1967, 100, 4027.

79. G. Lang and J. Vialle, Bull.Soc.chim. France, 1967, 2865.

80. J. Derocque and J. Vialle, Bull.Soc.chim. France, 1967, 3079.

81. J. Derocque, M. Perrier, and J. Vialle, Bull.Soc.chim. France, 1968, 2062.

82. E. Klingsberg, J.Org.Chem., 1968, 33, 2915.

83. H. Behringer and J. Falkenberg, Chem.Ber., 1969, 102, 1580.

84. F. Leung and S.C. Nyburg, Canad.J.Chem., 1971, 49, 167.

85. F. Leung and S.C. Nyburg, Chem.Comm., 1970, 707.

86. D.H. Reid and J.D. Symon, Chem.Comm., 1969, 1314.

87. A. Hordvik and K. Julshamn, Acta Chem.Scand., 1972, 26, 343.

88. R.J.S. Beer, D. Cartwright, R.J. Gait, R.A.W. Johnstone, and S.D. Ward, Chem.Comm., 1968, 688.

89. R.J.S. Beer and R.J. Gait, Chem.Comm., 1970, 328.

90. R.J.S. Beer, D. Cartwright, R.J. Gait, and D. Harris, J.Chem.Soc.(C), 1971, 963.

91. P.L. Johnson, K.I.G. Reid, and I.C. Paul, J.Chem.Soc.(B), 1971, 946.

92. K.I.G. Reid and I.C. Paul, J.Chem.Soc.(B), 1971, 952.

93. P.L. Johnson and I.C. Paul, J.Amer.Chem.Soc., 1969, 91, 781.

94. K.I.G. Reid and I.C. Paul, Chem.Comm., 1970, 329.

95. F.E. King and D.G.I. Felton, J.Chem.Soc., 1949, 274.

96. D. Paquer, M. Perrier, and J. Vialle, Bull.Soc.chim. France, 1970, 4517.

97. R.J.S. Beer, J.R. Hatton, E.C. Llaguno, and I.C. Paul, Chem.Comm., 1971, 594.

98. A. Hordvik, E. Sletten, and J. Sletten, Acta Chem.Scand., 1969, 23, 1377.

99. D.H. Reid, J.Chem.Soc.(C), 1971, 3187.

100. G. Traverso, Ann.Chim. (Italy), 1957, 47, 3.

101. E. Klingsberg, J.Amer.Chem.Soc., 1963, 85, 3244.

102. R.J.S. Beer, D. Cartwright, and D. Harris, Tetrahedron Letters, 1967, 953.

103. J. Bignebat and H. Quiniou, Compt.rend., 1968, 267, C, 180.

104. J. Bignebat and H. Quiniou, Compt.rend., 1969, 269, C, 1129.

105. J. Bignebat and H. Quiniou, Compt.rend., 1970, 270, C, 83.

106. F. Arndt and G. Traverso, Chem.Ber., 1956, 89, 124.

107. F. Arndt, Chem.Ber., 1956, 89, 730.

108. M. Mammi, C. Garbuglio, and A. De Pace, Acta Cryst., 1963, Appendix 54, 5.26

109. M. Stavaux and N. Lozac'h, Bull.Soc.chim. France, 1967, 3557.

110. L. Claisen and L. Meyerowitz, Ber., 1889, 22, 3273.

111. C. Ainsworth, Org.Synth., 1959, 39, 27.

112. K. Knauer, P. Hemmerich, and J.D.W. van Voorst, Angew.Chem.Internat.Edn., 1967, 6, 262.

113. G.A. Heath and R.L. Martin, Austral.J.Chem., 1970, 23, 1721.

114. G. Duguay, D.H. Reid, K.Q. Wade, and (in part) R.G. Webster, J.Chem.Soc.(C), 1971, 2829.

115. F. Challenger, E.A. Mason, E.C. Holdsworth, and R. Emmott, J.Chem.Soc., 1953, 292.

116. G.R. Pettit and L.R. Garson, Canad.J.Chem., 1965, 43, 2640.

117. G.T. Morgan and H.D.K. Drew, J.Chem.Soc., 1924, 125, 731.

118. J.P. Buckley, Internat.J.Appl.Radiation Isotopes, 1971, 22, 41.

119. P.O. Bethge, Analyt.Chim.Acta, 1954, 10, 310.

120. R. Willstätter and T. Wirth, Ber., 1909, 42, 1920.

121. R. Förster, F. Lange, D. Drossbach, and W. Seidel, Z. anorg.Chem., 1923, 128, 245.

122. O. Foss, Acta Chem.Scand., 1949, 3, 435.

123. E. Fromm and P. Ziersch, Ber., 1906, 39, 3599.

124. S.K. Mitra, J. Indian Chem.Soc., 1933, 10, 71.

125. Z. Reyes and R.M. Silverstein, J.Amer.Chem.Soc., 1958, 80, 6367 and 6373.

126. S.H.H. Chaston and S.E. Livingstone, Proc.Chem.Soc., 1964, 111.

127. S.H.H. Chaston, S.E. Livingstone, T.N. Lockyer, V.A. Pickles, and J.S. Shannon, Austral.J.Chem., 1965, 18, 673.

128. R.K.Y. Ho, S.E. Livingstone, and T.N. Lockyer, Austral.J.Chem., 1965, 18, 1927.

129. S.H.H. Chaston, S.E. Livingstone, and T.N. Lockyer, Austral.J.Chem., 1966, 19, 1401.

130. S.H.H. Chaston and S.E. Livingstone, Austral.J.Chem., 1967, 20, 1065.

131. R.K.Y. Ho, S.E. Livingstone, and T.N. Lockyer, Austral.J.Chem., 1966, 19, 1179.

132. R.K.Y. Ho, S.E. Livingstone, and T.N. Lockyer, Austral.J.Chem., 1968, 21, 103.

133. S.E. Livingstone, Quart.Rev., 1965, 19, 386.

134. R.K.Y. Ho and S.E. Livingstone, Austral.J.Chem., 1968, 21, 1781.

135. S.H.H. Chaston and S.E. Livingstone, Austral.J.Chem., 1967, 20, 1079.

136. R.K.Y. Ho and S.E. Livingstone, Austral.J.Chem., 1968, 21, 1987.

137. R.L. Martin and I.M. Stewart, Nature, 1966, 210, 522.

138. R. Beckett and B.F. Hoskins, Chem.Comm., 1967, 909.

139. D. Festal, O. Coulibaly, R. Pinel, C. Andrieu, and Y. Mollier, Bull. Soc.chim. France, 1970, 2943.

140. A. Furuhashi, K. Watanuki, and A. Ouchi, Bull.Chem.Soc. Japan, 1968, 41, 110.

141. G.A. Heath, R.L. Martin, and I.M. Stewart, Chem.Comm., 1969, 54.

142. H.C. Freeman, G.H.W. Milburn, C.E. Nockolds, P. Hemmerich, and K.H. Knauer, Chem.Comm., 1969, 55.

143. G.A. Heath, R.L. Martin, and I.M. Stewart, Austral.J.Chem., 1969, 22, 83.

144. C.G. Barraclough, R.L. Martin, and I.M. Stewart, Austral.J.Chem., 1969, 22, 891.

145. G.A. Heath and R.L. Martin, Chem.Comm., 1969, 951.

146. L.H. Briggs and L.D. Colebrook, J.Chem.Soc., 1960, 2458.

147. A. Ouchi, M. Hyodo, and Y. Takahashi, Bull.Chem.Soc. Japan, 1967, 40, 2819.

148. A. Ouchi, M. Nakatani, and Y. Takahashi, Bull.Chem.Soc. Japan, 1968, 41, 2044.

149. A. Furuhashi, T. Takeuchi, and A. Ouchi, Bull.Chem.Soc. Japan, 1968, 41, 2049.

150. A. Furuhashi, Bull.Chem.Soc. Japan, 1970, 43, 3604.

151. F. Pettilon and J.E. Guerchais, Bull.Soc.chim. France, 1971, 2455.

152. M.O. Breitman, Y.G. Borodko, T.A. Stolyarova, and A.E. Shilov, Bull.Acad.Sci., U.S.S.R., 1970, 889.

153. B. Bock, K. Flatau, H. Junge, M. Kuhr, and H. Musso, Angew.Chem. Internat.Edn., 1971, 10, 225.

154. J.P. Collman, Angew.Chem.Internat.Edn., 1965, 4, 132.

155. S. McKenzie and D.H. Reid, J.Chem.Soc.(C), 1970, 145.

156. A. Hordvik and K. Julshamn, Acta Chem.Scand., 1971, 25, 1895.

157. K.A. Jensen and U. Henriksen, Acta Chem.Scand., 1967, 21, 1991.

158. H. Prinzbach and E. Futterer, in "Advances in Heterocyclic Chemistry", ed. A.R. Katritzky and A. J. Boulton, Academic Press, New York and London, 1966, Vol. 7, p. 82.

159. H. Behringer and A. Grimm, Annalen, 1965, 682, 188.

160. A. Hordvik and K. Julshamn, Acta Chem.Scand., 1971, 25, 2507.

161. A. Hordvik, unpublished data.

162. O. Foss and S. Hauge, Acta Chem.Scand., 1963, 17, 1807.

163. S. Hauge, Acta Chem.Scand., 1971, 25, 1134.

164. S. Hauge, D. Opedal, and J. Aarskog, Acta Chem.Scand., 1970, 24, 1107.